Lincoln University
Te Whare Wānaka o Aoraki
CHRISTCHURCH•NEW ZEALAND

Lincoln University Digital Dissertation

The mobility of two emerging contaminants, gallium and indium, in the soil – plant system

---

A Dissertation

submitted in partial fulfilment

of the requirements for the Degree of

Bachelor of Science (Honours)

at

Lincoln University

by

Hayley Jensen

Lincoln University

2017

Abstract of a Dissertation submitted in partial fulfilment of the requirements for the Degree of Bachelor of Science (Honours).

The mobility of two emerging contaminants, gallium and indium, in the soil – plant system

by

Hayley Jensen

Gallium (Ga) and indium (In) are non-essential trace elements present at low concentrations in Earth's crust. They have a variety of applications, particularly in portable electronic devices such as mobile phones and portable computers. With increasing technological dependence, the risk of soil contamination is rising, through mining, extraction, and product disposal. Entry to the food chain could be detrimental to the health of humans and ecosystems. Relatively little is understood regarding behaviour in the environment, but both elements are believed to readily hydrolyse and precipitate in soil, with root retention further restricting movement into plant shoot biomass. This study aimed to determine the mobility of Ga and In in the soil-plant system.

Batch sorption experiments were completed to quantify the degree of retention to the soil matrix. Perennial ryegrass (*Lolium perenne* L.) was grown in spiked soil to measure the capacity for uptake and translocation to above-ground biomass. Hydrolysis models were produced with a numerical equilibrium speciation model to estimate the predominant species in solution, providing an aid to understand of the processes occurring.

Gallium and In were strongly retained by the soil matrix; distribution coefficients (K_d; measure of partitioning between solid and aqueous phases) averaged over a range of concentrations were approximately 400 and 2000 respectively. Mobility increased with pH (from pH 5.54-7.14, Ga K_d decreased 689-265 and In 1266-458), decreased with time, and relative mobility decreased with the concentration of Ga and In entering the system (Ga K_d increased 88-392 when application rose from 1-30 mg L^{-1}, though solution concentrations increased from 0.06-1.33 mg L^{-1}). Ga/$In(OH)_3$ precipitation is believed to largely contribute to the sorbed fraction, and increased dominance of the anion ($Ga(OH)_4^-$) is likely responsible for higher Ga mobility.

Low concentrations of both elements were present in shoot biomass; Ga reached 11.57 mg kg^{-1}, with In plateauing at 0.015 mg kg^{-1} in the highest two treatments. Relatively little of the total mass applied to soil was harvested, peaking at 0.013% Ga and 0.0021% In. Even when the fraction retained to the soil matrix was estimated, there was little movement from solution to shoots, hypothesised to be attributed to sorption to outer root cells.

Data showed that mobility of both elements were low, thus there is little risk of Ga and In contaminants entering the food chain via physiological uptake, though entry via other pathways such as atmospheric deposition (of aerosols, onto ingested foliage) cannot be ruled out. Strong retention in the upper soil profile is predicted. Future research is required to verify if these findings are applicable across a range of environmental conditions, along with the effect of other contaminants on soil mobility and plant uptake.

Keywords: gallium, indium, soil, mobility, retention, sorption, hydrolysis, precipitation, distribution coefficient, partitioning, bioavailability, plant uptake, contamination.

Acknowledgements

A huge thank you goes to my primary supervisor Brett Robinson and associate supervisor Niklas Lehto, for the opportunity and support to complete such an interesting honours project.

Thank you Leanne Hassell for being a huge help with the practical aspects.

I would also thank my parents for supporting me all these years, through the good, bad and stressful.

Finally, thank you Abigail for your never-ending advice, support and friendship here at Lincoln.

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

Gallium (Ga) and indium (In) are metallic trace elements. They have the atomic numbers 31 and 49 respectively, are present in group 13 of the periodic table, and predominantly form trivalent cations in solutions and complexes. There is no evidence that either element is essential for the completion of plant or animal life-cycles (Kabata-Pendias & Mukherjee, 2007; Ladenberger et al., 2015; Połedniok et al., 2012).

Gallium and In are present at low concentrations in Earth's crust, though elevated in sulphide deposits and Al-rich lithology. Crustal concentrations average at 15-19 mg kg^{-1} Ga, and 0.05-0.072 mg kg^{-1} In (Kabata-Pendias & Mukherjee, 2007; Lokanc et al., 2015). Both elements are chalcophilic (strongly lithologically associated with S and other chalcophiles (Reeder et al., n.d.)) and rarely form their own minerals, but readily substitute for elements of similar ionic radii with hydrothermal enrichment in sulphide mineral deposits (Wood & Samson, 2006). Indium is frequently found with Zn, Fe, Cu, Pb and Sn, with elevated concentrations in sphalerite (ZnS; 5-100, ≤10,000 mg kg^{-1}), chalcopyrite ($CuFeS_2$; 10-50, ≤1500 mg kg^{-1}) and stannite ores (Cu_2FeSnS_4; 5-500, ≤1500 mg kg^{-1}) (Schwarz-Schampera, 2014; Tolcin, 2017; Weeks, 1973; White & Hemond, 2012). Gallium is also frequently enriched in sphalerite (40-50, ≤10,000 mg kg^{-1}) with similar chalcophiles (Zn, Fe, Cu), but due to close similarities in ionic radii Al is the greatest determinant of Ga distribution (trivalent radii are 0.535Å and 0.620Å respectively (Shannon, 1976)). Gallium readily substitutes into aluminosilicate minerals, such as amphiboles, feldspars and micas, and bauxite is its greatest industrial source (10-812, average 57 mg kg^{-1}) (Butcher & Brown, 2014; Salminen, n.d.; Schulte & Foley, 2013; Weeks, 1973). Concentrations are low compared to Al and Fe (79,600 and 43,200 mg kg^{-1}), but Ga is of similar scale to associated trace elements (65 mg kg^{-1} Zn, 25 mg kg^{-1} Cu, 14.8 mg kg^{-1} Pb and 2.3 mg kg^{-1} Sn in the continental crust (Wedepohl, 1995)). Abundance is uneconomically low, thus Ga and In are extracted as by-products of other mining operations: In from Zn extraction (>95%) (Schwarz-Schampera, 2014; Tolcin, 2017), and Ga from Al extraction (~90%) (Rongguo et al., 2016; Schulte & Foley, 2013).

Gallium and In are used extensively in a variety of applications, predominantly industrial and electronic. Indium is predominantly utilized as the alloy indium-tin oxide (ITO); a highly transparent, heat reflective and electronically conductive compound used as thin-film coatings. ITO is present on liquid crystal displays (LCDs) (in televisions, portable computers and watches), plasma displays and touch screens. Indium is also used in semiconductors for photovoltaics/solar cells, light-emitting

diodes (LEDs) and laser diodes (LDs), along with frequent use in solders and fusible alloys for industrial processing (Cobelo-García et al., 2015; Ladenberger et al., 2015; Schwarz-Schampera, 2014; Waterlot et al., 2013). Gallium arsenide (GaAs) semiconductors are used extensively in wireless communications (e.g. mobile phones, GPS, wireless LAN) and optoelectronic applications (LEDs, LDs and infrared emitting diodes (IREDs) used in touch screens, night vision devices and solar cells). Gallium nitride (GaN) is frequently used in optoelectronic LEDs for televisions, portable electronic devices and lighting (Butcher & Brown, 2014; Maneesuwannarat et al., 2016a). Gallium nitrate and maltolate have the potential for pharmaceutical use (Babula et al., 2008; Bernstein, 2005). Many of these products are used on a daily basis in first-world countries.

Usage of Ga and In is increasing, which increases the risk of environmental contamination through extraction and product disposal. Technological advances and societal structure evolution has led to increased use and dependence on the electronic devices which utilize these elements. Global laptop and tablet shipments increased from 220 million units in 2010 to 404.38 in 2014 (Statista, 2017). Gallium arsenide consumption increased 6% in 2015, attributed to smartphone production (Jaskula, 2016), and primary Ga extraction also rose, from 78 to 280 tonnes in 2009-2013 (Bhavan, 2016). Consumption of primary In in the US increased from 30 to 120 tonnes 1991-2011 (Hines et al., 2013), and is expected to continue due to production of ITO-containing flat panel displays and solar cells (Ladenberger et al., 2015). Extraction (via mining and ore processing) is frequently responsible for elevated concentrations of Ga and In in the surrounding soil, water and air. Ha et al. (2011) recorded 3.3-96.7 mg kg^{-1} In in the soil at various sites surrounding a Zn-Pb sulphide mine (versus 0.85 mg kg^{-1} in a nearby uncontaminated site), from direct deposition of tailings to the surrounding land. Połedniok et al. (2012) observed elevated concentrations of Ga in soils surrounding Zn and Pb processing plants, with 437 & 382 mg kg^{-1} Ga versus 41.7, 109 and 218 mg kg^{-1} in agricultural areas. Ga and In have relatively low economic value ($400 and $240-340 kg^{-1} in 2016, versus $19773 kg^{-1} Pd and $40831 kg^{-1} Au (USGS, 2017)), and the mass in many products is small with a high cost of recycling. A mobile phone (105 g, 8% mass printed circuit board) may contain just 1.176 mg Ga, worth 0.047 cents (GSMArena, 2010; Luda, 2011; Oguchi et al., 2011; USGS, 2017). Thus many products are deposited into landfills from where they have the potential to leach into soil and water (Maneesuwannarat et al., 2016b). Associated compression and damage to casings increases the likelihood of liberation of the heavy metal constituents (Robinson, 2009). Steinberger (1998) calculated that damaged biospherically-exposed thin-film modules had the potential to increase soil In concentrations by 20 $\mu g\ kg^{-1}$.

Gallium and In contamination has the potential to have adverse effects on plant and animal health if these elements are able to enter the food chain. One of the most likely pathways for the entry of Ga and In to animals is oral ingestion of plant material, via physiological uptake from soil. Little

investigation has been conducted regarding the safety of these elements, thus there are no known food or drinking water limits (ESPI Metals, 2015; ESPI Metals, 2016). Although assumed to have low oral animal toxicity (Kabata-Pendias & Mukherjee, 2007; Salminen, n.d.b), a few cases of severe toxicity have been documented. Ivanoff et al. (2012) reported that entry of Ga-halide complexes produced various symptoms, including increased heart rate, tremors and black-outs in a healthy young female. Reductions to plant growth have also been observed; Yu et al. (2015) measured a 65% reduction in the relative growth rate of rice seedlings exposed to 15.42 mg L^{-1} Ga. However, for Ga and In to enter the plant system they must be bioavailable (capable of uptake in physiologically active forms (Hooda, 2010)). Solubility is a prerequisite of bioavailability, with the concentration of soluble forms determined by the degree of which Ga and In are removed from solution via precipitation or adsorption to the soil matrix.

Despite relatively little research into the behaviour of Ga and In in the soil - plant system, a few key processes have been identified. Gallium is naturally present at 3-70 mg kg^{-1} across a range of soil types, and In at 0.01-0.5 mg kg^{-1} (Kabata-Pendias & Mukherjee, 2007). In aqueous systems, both elements are acidic and undergo pH-dependant hydrolysis to the mononuclear species $Ga/In(OH)^{2+}$, $Ga/In(OH)_2^{+}$, $Ga/In(OH)_3^{0}$ and $Ga/In(OH)_4^{-}$ (Bernstein, 1998). $Ga/In(OH)_3$ is poorly soluble (K_{sp} of 1.3×10^{-34} and $10^{-36.9}$ reported for the In analogue (White & Hemond, 2012)) and readily precipitates, thus little Ga and In are present in the soil solution. Both elements are assumed to be capable of adsorbing to the soil matrix, analogous to other trace elements (Hooda, 2010). Distribution coefficients (measure of the fraction in the solid relative to aqueous phase) of 210 to 200,000 Ga, and 180 to 11,000 In have been calculated (Sheppard et al., 2007). Reported above-ground plant biomass concentrations range from below detection limit (Eriksson, 2001), to 6.6 mg kg^{-1} Ga (Dursun et al., 2006) and 3.89 mg kg^{-1} In (Ha et al., 2011). Both elements are strongly bound by pectin in the walls of outer root cells, restricting entry to the inner root and xylem, thus limiting translocation to shoot biomass (Eticha et al., 2005; Horst et al., 2010; Kopittke et al., 2009; Mauseth, 2014). Syu et al. (2017) calculated <0.47 shoot:root Ga and In concentrations in rice seedlings. Excessive availability have been shown to cause rhizotoxicity (0.90 μM Ga and 0.72 μM In in solution reduced cowpea root elongation rates by 50%, in a study by Kopittke et al. (2009)), with suggestion of amelioration via organic acid exudation (Chang et al., 2017). Gallium is capable of inducing Fe deficiencies, by substitution of Ga^{3+} for Fe^{3+} in Fe acquisition compounds (Babula et al., 2008).

However, the capacity for Ga and In soil contaminants to enter harvestable plant biomass remains relatively unknown. Some studies (Sheppard et al. (2007), Tyler & Olsson (2001) and Watmough (2008)) have quantified soil matrix retention, but in natural systems instead of contaminated, without an understanding on the effect of pH or concentration on the degree of retention. There is little translation of how chemical properties (e.g. tendency to hydrolyse) affect the physical and

chemical processes in soil. The capacity for Ga and In plant uptake across a range of concentrations or in agricultural species has been poorly documented (Syu et al. (2017), Yu et al. (2015), Eriksson (2001), Waterlot et al. (2013) are examples of the first and latter two respectively), with no research combining the two factors in a system where soil dynamics also influence plant uptake, to analyse the entire system. A quantification and understanding of Ga and In mobility is essential to evaluate if there is the potential for these elements to enter plant biomass at concentrations high enough to potentially pose risk to the health of humans and ecosystems, thus warranting further investigation, or whether contamination will lead to accumulation in the soil profile.

When aqueous forms are added to soil, it is hypothesised that Ga and In will be quickly retained by the soil matrix. Plant uptake and translocation to shoot biomass will be extremely low, with little risk of these elements leaving the system.

The aim of this study is to determine the mobility of Ga and In in the soil – plant system using experimentation and modelling. Batch sorption experiments were completed to investigate the capacity for retention to the soil matrix. Perennial ryegrass (*Lolium perenne* L.) was grown to measure the capacity for movement into shoot biomass. Data were extracted from a numerical equilibrium speciation model to aid interpretation of behaviour in the system.

Chapter 2

Background information

2.1 Forms and partitioning of gallium and indium in soil

2.1.1 Chemical properties

Gallium forms the two stable isotopes ^{69}Ga (60.4%) and ^{71}Ga (39.6%) and various radioactive isotopes (such as ^{66}Ga, ^{70}Ga and ^{73}Ga), with In as stable ^{113}In (approximately 4%) and extremely slowly decaying ^{115}In (96%, 4.41x10^{14} year half-life) (Audi et al., 2003; Salminen, n.d.; Salminen, n.d.b.).

Much of the behaviour of these elements is attributed to properties such as their ionic radii and electron configurations, thus are presented in Table 2.1.

Similarities to elements within the lower two sections is explanatory of geological associations. Ionic radius is particularly important, as the difference between elements must be ≤15% to enable the capacity for isomorphous substitution in mineral lattices (ions are only capable of replacing those of similar size, due to the tight network of atoms and bonds within the structure) (Ryan, 2014).

Table 2.1 Chemical properties of Ga, In and associated elements.

Element	Oxidation states *(main state)*[a]	Atomic mass[b]	Ionic radius (Å)[c]	Ionic potential (z/r)[f]	Electro-negativity[b]	Ionization energy (eV) (1st electron)[d]	Electron configuration	Electron configuration (ion)[e]
Gallium (Ga)	*+3*, +1, +2	69.723	Ga^{3+} 0.620	4.84	1.81	5.9993	[Ar] $3d^{10}$ $4s^2$ $4p^1$	[Ar] $3d^{10}$
Indium (In)	*+3*, +1, +2	114.818	In^{3+} 0.800	3.75	1.78	5.7864	[Ar] $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $5s^2$ $5p^1$	[Ar] $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$
Similarities in geological distribution, soil and physiological behaviour								
Aluminium (Al)	*+3*	26.982	Al^{3+} 0.535	5.61	1.61	5.9858	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^1$	$1s^2$ $2s^2$ $2p^6$
Iron (Fe)	*+3*, +2, +4, +6	55.847	Fe^{2+} 0.78	2.56	1.83	7.9025	[Ar] $4s^2$ $3d^6$	[Ar] $3d^6$
			Fe^{3+} 0.645	4.65				[Ar] $3d^5$
Similarities in geological distribution								
Zinc (Zn)	*+2*	65.39	Zn^{2+} 0.740	2.70	1.65	9.3942	[Ar] $3d^{10}$ $4s^2$	[Ar] $3d^{10}$
Copper (Cu)	*+2*, +1	63.546	Cu^{2+} 0.73	2.74	1.9	7.7264	[Ar] $4s^1$ $3d^{10}$	[Ar] $3d^9$
			Cu^{+} 0.77	0.77				[Ar] $3d^{10}$
Lead (Pb)	*+2*, +4	207.2	Pb^{2+} 0.86	2.33	2.33	7.4167	[Ar] $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ $5s^2$ $5p^2$ $5d^{10}$ $6s^2$ $6p^2$	[Ar] $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ $5s^2$ $5p^2$ $5d^{10}$ $6s^2$
Tin (Sn)	*+4*, +2	118.71	Sn^{4+} 0.690	5.80	1.96	7.3439	[Ar] $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $5s^2$ $5p^2$	[Ar] $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$

[a]Kabata-Pendias & Mukherjee (2007), 'main state' refers to the oxidation state most common in the environment (thus extremely stable in many forms); [b]Barbalace (2007); [c]Effective ionic radius for high spin (where applicable) atoms with VI coordination number (octahedral complex), Shannon (1976), documented for the most and extremely common oxidation states; [d]Martin et al. (2013); [e]For the main/common oxidation states; [f]Calculated from (main-or-common oxidation state/respective ionic radius).

2.1.2 Forms of gallium and indium in soil

2.1.2.1 Aqueous speciation

The aqueous chemistry of Ga and In is dominated by hydrolysis of poorly-soluble oxides/hydroxides. Gallium and In have the highest stability in the +3 oxidation state in aqueous solutions (Table 2.1), and form octahedral hydrated cations. Ga^{3+} and In^{3+} are acidic, and donate protons to form $Ga/In(OH)^{2+}$, $Ga/In(OH)_2^{+}$, $Ga/In(OH)_3^{0}$ and $Ga/In(OH)_4^{-}$ (stoichiometric hydrolysis is shown in Equation 2.1). $Ga/In(OH)_3^{0}$ is poorly soluble, therefore most precipitates to amorphous $Ga/In(OH)_3$(am), which ages to higher crystallinity GaO(OH)(c) and the In analogue. High temperatures and/or pressure in hydrothermal, geomorphic and industrial environments enable transformation to α-GaOOH, β-Ga_2O_3 and various other minerals (Pokrovski et al., 1997). Solubility product constants (K_{sp}) within literature are not consistent, decreasing with time and increasing with temperature. Modelling at 25°C, pH 2-10, in pure water has estimated that $10^{-9.3}$-10^{-2} M GaO(OH)(c)/α-GaOOH is capable of dissolution, and $10^{-7.3}$-10^{-1} M $In(OH)_3$(c) with K_{sp} in the range of 1.6^{-40}-1.3^{-34} reported (Bernstein, 1998; Wood & Samson, 2006). Gallium and In precipitates are amphoteric, capable of accepting and donating protons. $Ga/In(OH)_4^{-}$ is tetrahedral, but the other mononuclear ions are octahedrally coordinated. Various polynuclear species (such as $[GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ and $In_4(OH)_6^{6+}$) are also present, but less of their chemistry is understood due to measurement difficulties (Pokrovski et al., 2002; Wood & Samson, 2006). With the exception of various crystalline compounds, forms of Ga, In and Al are analogous (Greenwood & Earnshaw, 1984).

$$Ga(H_2O)_6^{3+} + H_2O \leftrightarrow Ga(H_2O)_5(OH)^{2+} + H_3O^+$$
$$Ga(H_2O)_5(OH)^{2+} + H_2O \leftrightarrow Ga(H_2O)_4(OH)_2^{+} + H_3O^+$$
$$Ga(H_2O)_4(OH)_2^{+} + H_2O \leftrightarrow Ga(H_2O)_3(OH)_3^{0} + H_3O^+$$
$$Ga(H_2O)_3(OH)_3^{0} + H_2O \leftrightarrow Ga(H_2O)_2(OH)_4^{-} + H_3O^+$$

Equation 2.1 Acidic hydrolysis equations for Ga (Bernstein, 1998).

pH is determinant of the aqueous forms present, thus has a strong influence on the solubility of Ga and In. Within an aqueous system at 25°C, the dominant Ga species are Ga^{3+} at pH <3, $Ga(OH)^{2+}$ at approximately 3-4, and $Ga(OH)_4^{-}$ >5-6. In^{3+} dominates at pH <4, $In(OH)_3$ at 5-9, and $In(OH)_4^{-}$ at >9.5 (Figure 2.1) (Bénézeth et al., 1997; Diakonov et al., 1997; Kabata-Pendias & Pendias, 2001; Wood & Samson, 2006). The lesser-charged cations have a lower frequency and stability, partially due to the high dielectric constant of water (Bénézeth et al., 1997). Solubility is lowest when formation of $Ga(OH)_3$ and $In(OH)_3$ and thus precipitation peaks. Bernstein (1998) reported a minimum total Ga

solubility of $10^{-7.2}$M at pH 5.2, and Wood & Samson (2006) $10^{-9.3}$M at pH 4.3, in pure water at 25°C. $10^{-7.3}$ was the lowest for In, spanning across pH 4.5-9, reflective of the dominance of $In(OH)_3$ (Wood & Samson, 2006).

The ability to hydrolyse, and differences between Ga, In and Al, is attributed to their ionic potential and strength of the effective nuclear charge. Hydrolysis occurs when the δ^- O atom in a surrounding water molecule is highly electrostatically attracted to the metal cation, decreasing the Me-O bond length, repelling the δ^+ H atom and reducing the quantity of energy required to break the bond (Barysz et al., 2004). These 3 elements have high oxidation states and relatively small ionic radii, allowing them to readily hydrolyse, however Ga is more acidic than Al and In (pK_a values of 2.6, 5.0 & 3.9 respectively (Grzybkowski, 2006)). Gallium has a higher effective nuclear charge than Al (Ga^{3+} contains a d^{10} orbital which provides lesser shielding than the s and p orbitals in Al^{3+} (Greenwood & Earnshaw, 1984)) and smaller ionic radius than In (0.620 versus 0.800Å (Table 2.1)), which causes the nucleus to be more polarizing. Therefore, a larger fraction Ga is hydrolysed to the anionic form within particular pH range. This is responsible for differences in species and soil partitioning, restricting the use of Al as an analogue to explain behaviour.

$Ga(OH)_4^-$ is expected to be the dominant species in the soil solution, with In predominantly as $In(OH)_2^+$ and $In(OH)_3^0$. Most soils are pH 4-8 (Hooda, 2010), with 5.5-7.0 generally optimal for plant growth (and thus predominant in agricultural systems) (DeSutter & Godsey, 2010; McLaren & Cameron, 1996), equating to those species on the model in Figure 2.1. However due to the lower soil temperature in many temperate climates (e.g. 7.6-15.2°C across New Zealand (NIWA, n.d.)), larger fractions of less hydrolysed species are expected in many soils, particularly the trivalent cation. Other ligand species are not accounted for.

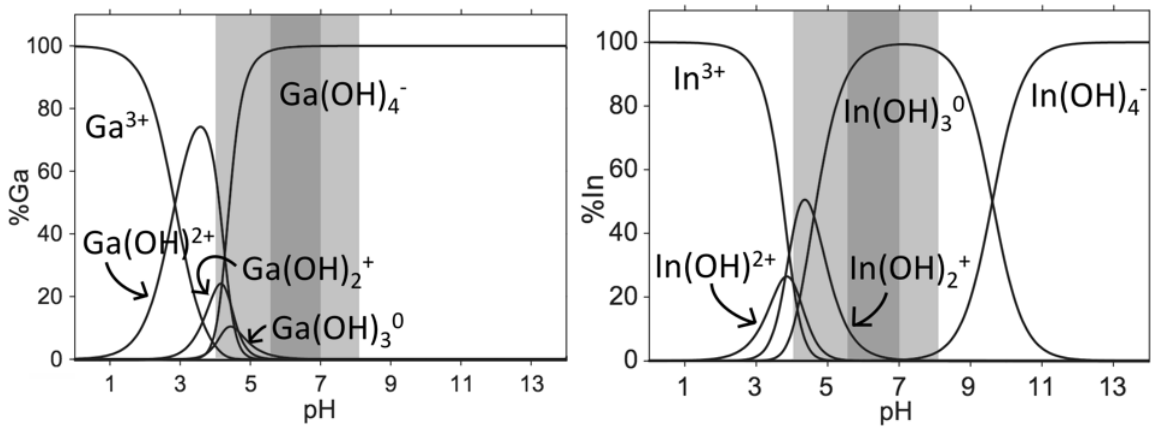

Figure 2.1 Monomer speciation of Ga and In in aqueous systems, from Wood & Samson (2006). Light grey and dark grey segments indicate standard (pH 4-8) and optimal (pH 5.5-7) soil pH ranges. Model formed at 25°C in pure water.

2.1.2.1.1 Types of ligand associations

2.1.2.1.1.1 Inorganic ligands

Gallium and In may bind to various inorganic anions, particularly halides, when availability is not limiting. Gallium forms stable F^-, SO_4^{2-} and $PO_4^{3=}$ compounds, while In predominantly complexes with Cl^-, F^- and HS^-. These compounds are usually rare in the soil system, due to the low abundance of Ga and In, competition from other elements (e.g. Al^{3+}, Na^+, Ca^{2+}, K^+ & NH_4^+) and high availability of water as a competing ligand. Indium chloride complexes are believed to be relatively abundant in natural systems, especially at high concentrations of Cl^- or low OH^-; $InCl^{2+}$ and $InCl(OH)^+$ have been particularly frequently documented (Kabata-Pendias & Mukherjee, 2007; Kopittke et al., 2009; Ritchie & Raghupathi, 2008; Wood & Samson, 2006). Less is understood regarding anionic inorganic complexes; little stability constant data has been recorded (Tuck, 1983; Wood & Samson, 2006). Few literature pieces refer directly to soils. Complexation is assumed to be dependent on the availability of other elements in the system, and increases total solubility through removal of pure ionic forms (Wood & Samson, 2006).

Differences in complexation are attributed to the hardness of the cations. Both elements are classified as hard acids (dense electron clouds with low polarizabilities), which predominantly bind with hard bases such as oxygen-containing groups (hydroxide and carboxylate) and halogens (Pearson, 1963; Stumm & Morgan, 2009; Wood & Samson, 2006). However, In is softer; In^{3+} has a larger ionic radius (0.800 Å) than Ga^{3+} (0.620 Å), valence electrons are further away with less electrostatic attraction to the nucleus, and binding is less ionic/polar. Complexes with similarly softer bases such as Cl^- and HS^- have greater stability than Ga analogues.

2.1.2.1.1.2 Organic ligands

A large portion of Ga and In is complexed with dissolved organic matter. Forms vary, though acetic, oxalic, malic and citric organic acids, rich in hydroxyl and carboxyl groups, have been frequently reported in literature (Boros et al., 2014; Chang et al., 2017; Ritchie & Raghupathi, 2008; Salminen, n.d.b). The short chain length (2-6 C) and high hydroxide content (O/C 1-1.25) causes these molecules to be highly soluble, and are released through root exudation (Chang et al., 2002). Organic acids have a high capacity to form stable multi-dentate complexes. Bernstein (2005) reported that citrate is effective at reducing hydrolysis and formation of insoluble $Ga(OH)_3$ compounds.

2.1.2.2 Non-aqueous speciation

2.1.2.2.1 Precipitation

A large fraction of Ga and In is in the form of precipitated hydroxides, though other insoluble compounds may be formed. $Ga(OH)_3^0$ and $In(OH)_3^0$ are readily formed from hydrolysis in a typical

agricultural soil pH range, but are poorly soluble thus excess readily precipitates. Crystallinity increases and dissolution potential decreases with aging, heat and pressure (Bernstein, 1998; Ladenberger et al., 2015). Other precipitates such as $GaPO_4$, In_2S_2, and $In(CO_3)_3$ have been reported (Bernstein, 1998; Salminen, (n.d.b), and are also deemed poorly soluble (K_{sp} of $10^{-73.24}$, 10^{-15}, and 10^{-25}-$10^{21.63}$ were measured for In_2S_3, $In_2(CO_3)_3$ and $InPO_4$ respectively (White & Hemond, 2012)). In particular, precipitation as sulphide minerals in anoxic conditions is highly likely, due to the chalcophilic behaviour of both elements (Alloway, 2013; Kabata-Pendias & Mukherjee, 2007).

2.1.2.2.2 Soil colloidal sorption

Four types of colloid sorption are believed to occurs. Trivalent cations undergo hydrolysis to various extents within the pH range predominant of soils (versus divalent, at pH 6 – 12 (Grzybkowski, 2006)), thus analogues cannot fully explain the behaviour of Ga and In within this section.

2.1.2.2.2.1 Outer-sphere adsorption

Frequency and strength of outer-sphere binding depends on the speciation of hydrolysed Ga and In, though is generally of low importance to trace elements. Outer-sphere adsorption consists of electrostatic attractions between superficial colloidal functional groups (silanol, inorganic hydroxide or organic) and oppositely charged hydrated ions (Bradl, 2004; Ryan, 2014). The size of this fraction is pH dependent, due to its role in the types of Ga and In hydroxyl speciation, and its determination of the charge of amphoteric functional groups (especially on Fe and Al hydroxides (McLaren & Cameron, 1996)). Hypothetical explanations can be made, though there is a lack of adequate literature for validation. When present, Ga^{3+} and In^{3+} should theoretically form strong bonds and be poorly affected by competition from other elements. Indium sorption is likely low in most soils; exchange site protonation limits its mono and divalent forms in acidic soils, with precipitation of $In(OH)_3$ limiting as the pH rises. Gallium is hypothesized to sorb well to anion exchange sites in most soils, though the anion exchange capacity (AEC) decreases as the pH and deprotonation increases. McLaren & Cameron (1996) claim that macronutrients outcompete and severely limit outer-sphere adsorption by trace elements, due to concentration differences; thus other adsorption mechanisms are more determinant of Ga and In behaviour.

2.1.2.2.2.2 Inner-sphere/specific adsorption

Specific adsorption consists of a complex involving one or multiple chemical bonds between a dehydrated ion and a functional group, and is poorly reversible. The ion may be directly bound to the surface oxygen atom, often causing deprotonation (chemisorption) or may replace a (predominantly hydroxyl) superficial function group (ligand exchange) (Bradl, 2004; Goldberg, 1997; Shaheen et al. (2013). Uncertainties remain regarding various characteristics of Ga and In sorption, including the species adsorbed from solution at normal soil pH ranges; the pH range at which sorption occurs; the

effect of hydrolysis on sorption, and whether Ga is specifically adsorbed as an anion. Fischer et al. (2007) reported that Al was specifically adsorbed as $Al(OH)^{2+}$ instead of its trivalent cation, with adsorption starting at the pH it began to be formed. Shaheen et al. (2013) state that Cu adsorption increases with the formation of the $CuOH^-$ speciation, due to its stronger binding than Cu^{2+}. Lin et al. (1997) recorded the formation of monodentate $SO(Ga/In)OH^+$ and bidentate $(SO)_2(Ga/In)^+$ complexes on goethite, which occurred at a higher pH for In, but the pH ranges in the study (1.5-4.0) were much lower than most natural soils, with only trivalent cations involved. Adsorption of TEs generally increases with pH, due to the increasingly negative net charge and associated electrostatic attraction (increased ease of binding and site proximity), but $Ga(OH)_4^-$ may induce repulsion and decrease its sorption capacity. Hooda (2010) reported that anions such borate (BO_3^{3-}) could specifically adsorb through ligand exchange, but anion adsorption decreases with pH, therefore it is unknown whether most soils have the capacity to specifically adsorb large quantities of $Ga(OH)_4^-$ when it is predominantly present.

2.1.2.2.2.3 Occlusion and absorption

Gallium and In are theoretically susceptible to occlusion and absorption into the soil matrix. No literature was uncovered discussing these processes in respect to Ga and In directly, thus there is also no information indicating behavioural differences to other trace elements. Both processes utilize ions which have become specifically adsorbed; weathering-induced mineral dissolution is required to release these, and allow movement.

2.1.3 Partitioning of gallium and indium in soil

Within the soil profile, Ga and In are present in solution, precipitated, or partitioned between four distinct soil matrix fractions via various sorption types. The aqueous fraction is also inclusive of outer and weakly inner-spherically sorbed species, as they form a bioavailable dynamic equilibrium with the concentration in the soil solution. Manganese and Fe hydrous oxides are abundant in the profile, capable of occlusion and absorption in addition to adsorption, due to their redox dynamic behaviour. As there is evidence of plant uptake (Table 2.6 and Table 2.7), Ga and In are present within, along with adsorption to organic material. Their chalcophilic behaviour is responsible for an association with parent and neoformed sulphide minerals. Both elements are capable of sorbing to, though Ga is more prone to originating from aluminosilicate minerals. Połedniok (2012) measured the partitioning of Ga, and Boughriet et al. (2007), Hou et al. (2005) and Waterlot et al. (2013) measured In in a variety of environments.

In most environments, the fraction associated with the soil matrix far exceeds the aqueous fraction. The distribution coefficient, K_d, is a quantification of the partitioning of an element between the soil matrix/soil phase and solution, used to compare the strength of retention and mobility between

different elements and environmental conditions. Though relatively few, reported K_d values range from 880-1,999,999 for Ga, and 180-11,000 for In (Table 2.4 and Table 2.5). Other studies, such as Hou et al. (2005), also measured partitioning and although the sensitivity of presented data was too low for calculation of distribution coefficients, 53-78% Ga and 40.5->99% In was unavailable to plants (Table 2.2 and Table 2.3).

Table 2.2 Compilation of measured Ga soil solution/exchangeable fractions.

Study	Compared variable	Categories	Fraction sorbed to soil matrix (%)	Elemental source
Połedniok (2012)	Location, soil type and pH	Industrial, brown, weakly acidic-neutral	78	Contamination
		Agricultural, white, acidic	53	Natural
Połedniok et al. (2012)	Location	Industrial	71	Contamination
		Agricultural	67	Natural

Table 2.3 Compilation of measured In soil solution/exchangeable fractions

Study	Compared variable	Categories	Fraction sorbed to soil matrix (%)	Elemental source
Hou et al. (2005)	Soil type	Andosol	68-97	Spiked 18 months prior
		Cambisol	>96	
		Fluvisol	>99	
		Regosol	>92	
Boughriet et al. (2007)	Range of soil types		>97	Contamination
Waterlot et al. (2013)	Soil use	Kitchen garden (food production)	40.5-94.5	Contamination
		Lawn (recreational)	>95	

Table 2.4 Compilation of measured Ga and In distribution coefficients.

Study	Compared variable	Categories	K_d	Elemental source
Tyler & Olsson (2001)	pH	5.4	219,779	Natural
		7.1-7.8	1,999,999	
Watmough (2008)	pH	3.8	2000	Natural
		7	100,000	
Tyler & Olsson (2002)	Range of soil types		14211	Natural
Sheppard et al. (2009)	Soil type	peat, fen	1300	Natural
		peat, former fen	7800	
		sandy till, oak forest	5900	
		clay gyttja, fen	9400	
		clay gyttja, open fen	7800	
		clayey till, fen	2600	
		clayey till, arable	14,000	
	Statistical value (from separate data)	Mean	13,000	Natural
		5th percentile	880	
		95th percentile	110,000	
Sheppard et al. (2007)	Statistical value	Mean	11,000	Natural
		Minimum	210	
		Maximum	200,000	

Table 2.5 Compilation of measured Ga and In distribution coefficients.

Study	Compared variable	Categories	K_d	Elemental source
Tyler & Olsson (2002)	Range of soil types		967	Natural
Sheppard et al. (2007)	Statistical value	Mean	2800	Natural
		Minimum	180	
		Maximum	11,000	

2.1.4 Soil factors affecting concentrations of gallium and indium in solution

2.1.4.1 Soil solution pH

pH is a large influencing factor on Ga and In adsorption and precipitation. Most trace element cations decrease in solubility with increasing pH, but due to the amphoteric properties of Ga and In and anionic presence in the normal soil range (particularly Ga), this assumption may not fully apply. This factor is naturally and anthropogenically dynamic.

Hydroxide precipitation is pH dependent, and responsible for increased bioavailability at extreme pH ranges. As the pH increases, hydrogen ions in $Ga/In(H_2O)_6^{3+}$ are more prone to separation, with attraction to increasing concentrations of OH^-, thus more hydrolysis occurs. Amphoteric trihydroxide is particularly stable and precipitates; above and below its peak occurrence the concentration of aqueous Ga and In increases. Wood & Samson (2006) modelled that increasing the pH from 5.5 to 7 increased total Ga solubility from approximately $10^{-8.3}$ to $10^{-7.1}$ M, in a 25°C aqueous system.

Sorption is expected to increase with increasing pH, with associated decreasing bioavailability, though the exact dynamics remain unclear. Precipitation of Fe and Al (Fe >3.5, Al >5.5) (Hooda, 2010) increases the quantity of binding sites, and decreases competition for those sites (along with less H^+), decreasing solution concentrations. Deprotonation of hydroxide groups (predominantly on humus, Fe/Mn hydrous oxides and aluminosilicate clay edges) increases with pH, increasing the negativity of the net colloidal charge (Alloway, 2013). In cationic forms this causes outer-sphere adsorption, and attraction for proximity to aid initiation of specific adsorption, to increase, decreasing solution concentrations. As $In(OH)_4^-$ formation occurs at a higher pH range, it is expected to behave similarly to many other trace elements and predominantly decrease in availability. Gallium has the competing processes of increased cation and decreased anion sorption, with the later process potentially leading to an increase in availability in non-acidic soils.

Only a couple of studies demonstrated differences in Ga and In soil behaviour with pH. Tyler & Olsson (2001) showed a large decrease in soil solution Ga as the pH rose from 5.2 – 7.8, however the gradient was relatively gentle and levelled out at high pH values. Little explanation was offered, but Al and Fe were also shown to decrease in concentration via precipitation, which is likely to be partially responsible. Ritchie & Raghupathi (2008) discovered that increasing the pH from 3 to 6 removed toxicity to wheat cells, as Ga was hydrolysed to less phytotoxic speciation.

2.1.4.2 Redox potential and dissolution

The redox potential of the soil solution does not directly affect Ga and In, but reduction and oxidation of other elements is responsible for dissolution or formation of compounds associated with Ga and In, thus influencing aqueous concentrations.

Both Ga and In are stable in only the +3 oxidation state in aqueous solutions. The monovalent state is also possible in soil, though details of its compounds and formation were not uncovered (Boros et al., 2014; Ladenberger et al., 2015). Standard electrode potentials show favoured formation of the trivalent states (trivalent: +0.56V Ga & +0.34V In, monovalent: no appropriate value Ga, +0.18V In) (Greenwood & Earnshaw, 1984). Changes in the soil redox potential will have no effect on the oxidation states of these two elements.

Iron and Mn are sensitive to changes in the redox potential, with dissolution of Fe and Mn hydrous oxides and increased solution Ga and In in anoxic soils. At redox potentials bellow 100 – 200 mV and -100 - -200 mV, Mn^{4+} and Fe^{3+} respectively are reduced to their divalent oxidation states. These have much higher solubility, thus dissolving the precipitates and releasing the compounds contained or adsorbed into solution. (Alloway, 2013; Hooda, 2010). A large fraction of Ga and In is associated with these elements. Fe^{2+} and Mn^{2+} also increase competition for sorption sites. When the redox potential rises, reprecipitation and adsorption occurs (if elements are still available). Less amorphous compounds have lower sensitivities to redox changes.

In extremely anoxic soil, formation of sulphides decreases solution Ga and In. Sulphur is relatively stable in its +6 oxidation state, and sulphide minerals readily oxidise to form high-solubility sulphate compounds upon expose to oxygen and water, above 0 - -150 mV (Alloway, 2013). Insoluble sulphide compounds reform below that threshold, with various elements (including Ga and In) bound in the structure. However, this is reliant upon the availability of S; most S is stabilized in organic matter (>90%) and sulphate is poorly retained by soil colloids thus leached (McLaren & Cameron, 1996).

Overall, the concentration of Ga and In in the soil solution increases with decreasing redox potential, but the extent of this increased availability is dependent on other elements and the environment. Dissolution of Fe and Mn hydroxide oxides generally occurs before sulphide mineral formation. A subsequent decrease in availability requires S, a long period of anaerobic conditions, and a lack of other suitable electron acceptors remaining. The response of Ga and In to redox is similar to many other trace elements, except for the increased chalcophilic affinity for sulphides. Soil redox potential usually poses little significance, except in particularly wet weather or poor-draining soils.

2.1.4.3 Parent material supply

The material the soil is formed from-elemental composition and ease of weathering-predominantly determines the total quantity of Ga and In which can potentially be released into the soil solution, in uncontaminated enviroments. Trace elements may also be naturally added through atmospheric deposition via forest fires and volcanic eruptions (Hooda, 2010), but both are believed to not add much Ga and In to soil (lack of inclusion in literature, and low concentrations in air in non-urban areas (<0.14 ng m^{-3}) (Kabata-Pendias & Mukherjee, 2007)). Particularly high concentrations of In are found in soils overlying sulphide mineral deposits, and Ga in Al-rich soil. Topsoil and source-rock Ga concentrations varied by less than 37% in 11/15 Californian soils sampled by Shiller & Frilot (1996). Ladenberger et al. (2015) demonstrated that throughout Europe, elevated In concentrations were closely related to ZnS mineral deposits in the underlying lithology.

2.1.4.4 Colloidal chemical composition

The composition of the colloidal phase is determinant of the quantity and capacity of binding sites to adsorb Ga and In, and is thus highly determinant of the amount of these elements present in the soil solution. These two factors can frequently qualitatively describe much of the variation in partitioning between soil types, such as that observed in Hou et al. (2005) when the allophane-rich Andosol retained more In than the Cambisol, Fluvisol and Regosol.

Finer textured soils have a larger colloidal surface area and are able to remove more Ga and In from the soil solution. As the surface area increases, the quantity of superficial functional groups able to outer-spherically and specifically adsorb various ions also increases. Coarser textured soils may have a higher capacity for absorption, but this process is relatively slow and requires space inside the mineral matrix for elements to diffuse into. Short-range-order amorphous aluminosilicate allophane and imogolite have proportionally large surface areas, at $\geq$200-300 $m^2 g^{-1}$, compared to crystalline compounds at just 15-70 $m^2 g^{-1}$ (Violante et al., 2005). Banin et al. (1981) reported significant decreases in grass uptake for multiple elements as the clay content and thus surface area increased (e.g. Cd concentrations were 0.75, 0.58 and 0.37 mg kg^{-1} in soil containing 6.5, 16.6 and 33.7% clay respectively).

The point of zero net charge (pzc) determines the capacity of the colloidal fraction to adsorb Ga and In, and varies across constituents. Pzc is the pH where the sum of the positive and negative charges on a compound equates to zero. Dissociation constants of hydroxyl and carboxyl groups vary across different compounds, due to the arrangement of atoms and bonds (Bradl, 2004). Compounds with low pzcs readily deprotonate with high cation adsorption, therefore decreasing the bioavailability of Ga and In when the pH is low, increasing when high, with a higher retention of less-anionic In. Organic matter and Mn hydrous oxides have low points of zero charges (2-4 and 1.5-4.6 respectively (Alloway, 2013; Qin et al., 2015) while Fe and Al oxides are generally higher (7-9.5 and 8-9.2 (Violante et al., 2005)), such as allophane, goethite and gibbsite at approximately 5, 6-7 and 10 respectively (Ryan, 2014). Bénézeth et al. (1997) pointed out that goethite (pzc 7.8) had a higher capacity for Ga sorption than kaolinite (pzc 4.6), above pH 4.5 when a large fraction was present as $Ga(OH)_4^-$.

2.1.4.5 Other soil factors

Soils are complex systems, and many other factors influence the concentration of Ga and In in solution. Competition from other elements limits sorption and increases availability, particularly when these elements are present as low valency speciation. Precipitation/dissolution with pH alters the quantity of binding sites and competition. Climate is determinant of the rate at which Ga and In are released via dissolution, and leached down the soil profile. The microbial population is able to drastically modify the behaviour of almost any element, through production of compounds to

increase or decreasing availability depending on physiological requirements, and is concentrated near the rhizosphere. Total organic matter content is of high importance for many soil properties, and increases the retention of cationic Ga and In.

2.2 Physiological plant uptake of gallium and indium

There is there is no evidence that Ga and In are essential or have a physiological role (Kabata-Pendias & Mukherjee, 2007; Ladenberger et al., 2015; Połedniok et al., 2012), but there is a small amount of data showing that low concentrations can be taken up by plants; this has been compiled in Table 2.6 and Table 2.7. Up to 30 mg kg^{-1} Ga has been reported in natural systems, and 3.89 mg kg^{-1} In. Ga^{3+} and In^{3+} are generally accepted to be bioavailable (Tyler, 2004a), but there is a lack of literature comparing aqueous species.

Table 2.6 Reported concentrations of Ga in plant material (natural and experimental systems).

Species	Concentration (mg kg^{-1} DM)	Contamination?	Reference
Above-ground; natural			
Wheat grain	<0.001	Possibly-sewage sludge	Eriksson (2001)
Barley grain	0.0010	Possibly-sewage sludge	Eriksson (2001)
European beech leaves	0.031-0.032	Highly likely-atmospheric deposition	Tyler (2005)
Hylocomium Splendens (glittering woodmoss)	0.14-16 (average 1.1)	-	Berg & Steinnes (1997)
10 various wild Vietnam species (shoot biomass)	0.36-3.38 (average 1.3)	Yes, Pb-Zn mine	Ha et al. (2011)
Wild edible mushrooms	1.4-6.6	-	Dursun et al. (2006)
Above-ground; experimental			
Rice	≤74	-	Syu et al. (2017)
Rice	≤48		Yu et al. (2015)
Possibly below-ground			
Various Soviet Union native species	0.02-5.5	-	Gribovskaya et al., 1978, as cited in Kabata-Pendias & Pendias, 2001, p. 196
Various	0.05-5	-	Połedniok et al. (2012)
Ectomycorrhizal European beech roots	0.06	-	Tyler (2004a)
10 various wild Vietnam species (root biomass)	0.52-6.43 (average 3.47)	Yes, Pb-Zn mine	Ha et al. (2011)

Various US native species	3-30	-	Shacklette et al., 1978, as cited in Kabata-Pendias & Pendias, 2001, p. 196

Table 2.7 Reported concentrations of In in plant material (natural and experimental systems).

Species	Concentration (mg kg^{-1} DM)	Contamination?	Reference
Above-ground; natural			
Wheat and barley grain	<0.005	Possibly-sewage sludge	Eriksson (2001)
European beech leaves	0.0002	Highly likely-atmospheric deposition	Tyler (2004a)
Fruit tree and tomato leaves	0.00064-0.0018	-	Fergusson, 1990, as cited in Kabata-Pendias & Mukherjee, 2007, p. 344
Lettuce leaves	0.004	-	Waterlot et al. (2013)
Ryegrass shoots	0.0065	-	Waterlot et al. (2013)
Lettuce leaves	0.0119-0.015	Yes-near previous smelter	Waterlot et al. (2013)
Ryegrass shoots	0.0161-0.0509	Yes-near previous smelter	Waterlot et al. (2013)
Various grasses	0.08-2.1 (FW)	Yes-unrinsed from industrial areas	Połedniok (2007)
10 various wild Vietnam species (shoot biomass)	0.14-3.89 (average 1.13)	Yes, Pb-Zn mine	Ha et al. (2011)
Above-ground; experimental			
Rice	≤151	-	Syu et al. (2017)
Possibly below-ground			
Ectomycorrhizal European beech roots	0.0008	-	Tyler (2004a)
Various	0.03-0.07	-	Połedniok (2007)
Various vegetables	0.03-0.71	-	Fergusson, 1990, as cited in Kabata-Pendias & Mukherjee, 2007, p. 344
Beets	0.08-0.3	-	Fergusson, 1990, as cited in Kabata-Pendias & Mukherjee, 2007, p. 344
10 various wild Vietnam species (root biomass)	0.28-1.59 (average 0.729)	Yes, Pb-Zn mine	Ha et al. (2011)
Various	1-2	-	Kabata-Pendias & Mukherjee (2007)

2.2.1 Shoot:root partitioning

Translocation of Ga and In above-ground is low, due to strong retention within root biomass. Due to their large ionic potentials, trivalent forms of both elements bind strongly to and are retained by de-esterified carboxylate groups in pectin (a cell-wall component) in epidermal and outer cortex (outer root) cells, severely restricting movement through the root and into the xylem (the pathway for shoot transport) (Eticha et al., 2005; Horst et al., 2010; Kopittke et al., 2009; Mauseth, 2014). This process is non-specific, and analogous to Al and other strong cations (e.g. La^{3+}, Gd^{3+}, Sc^{3+} and Ru^{3+}) (Kopittke et al., 2009).

Few studies have compared the partitioning of Ga and In between shoot and root biomass. Accessible data is compiled below (Table 2.8 and Table 2.9). Up to 9.73 was calculated from Ha et al. (2011), but data are too few to concede if this is a severe anomaly; that study compared species which were naturally found on, thus may have adapted to, the high Ga and In soil.

Table 2.8 Reported Ga shoot:root plant concentration ratios (natural and experimental systems).

Species	Shoot:root	Contamination?	Reference
Naturally observed			
Barley/wheat stem	0.0279	-	Sheppard et al. (2011)
10 various wild Vietnam species	0.0578-1.71 (average 0.549)	Yes, Pb-Zn mine	Ha et al. (2011)
Experimental			
Arabidopsis thaliana	0.082-0.223	-	Chang et al. (2017)
Rice	<0.01-0.47	-	Syu et al. (2017)
Rice	0.0183	-	Yu et al. (2015)

Table 2.9 Reported In shoot:root plant concentration ratios (natural and experimental systems).

Species	Shoot:root	Contamination?	Reference
Naturally observed			
10 various wild Vietnam species	0.174-9.73 (average 2.24)	Yes, Pb-Zn mine	Ha et al. (2011)
Experimental			
Rice	<0.01-0.44	-	Syu et al. (2017)

2.2.2 Gallium and indium phytotoxicity

High bioavailability of Ga and In can cause reductions to root growth, produce root lesions/ruptures, and reduce the maximum above-ground biomass, though due to a lack of studies there is no consensus on the thresholds which cause this behaviour. Symptoms and thresholds of toxicity are summarised in Table 2.10 and Table 2.11. Accumulation of Ga and In in the outer root cells near the meristem (root tip, where growth occurs) causes rigidification, reducing elongation rates, and lesions

form from the force of inner cells expanding faster than outer (Kopittke et al., 2009). Water and nutrient accessibility is thus reduced. As trivalent cations bind the strongest and analogous Al toxicity is only susceptible in acidic soil, Ga^{3+} and In^{3+} are believed to be the predominant phytotoxic speciation (Ishikawa et al., 1996; Kinraide, 1997). Toxicity via Ga/In_{13}^{7+} (and other >2+ valency polynuclear species) is limited by concentration (Kopittke et al., 2016). However, weakly anionic analogous $Al(OH)_4^-$ has also reportedly caused toxicity, at a high pH range as the dominant species (Brautigan et al., 2012). Though this is the most likely mechanism behind symptoms in Table 2.10 and Table 2.11, other processes cannot be ruled out.

Table 2.10 Reported Ga toxicity symptoms and thresholds, in various plant species.

Species	Symptoms	Lowest concentration	Notable concentrations	Reference
Arabidopsis thaliana (thale cress)	Reduction in root elongation, root fresh weight and shoot fresh weight.	6 μM Ga in solution, no soil; lowest concentration.	30 & 60% reduction in root length at 250 & 500 μM Ga.	Chang et al. (2017)
Onion	Reduction in root elongation and mitosis.	6×10^{-4}M $GaCl_3$ (only concentration used).	Root elongation stopped after 6-9 hours.	Clarkson (1965)
Cowpea	Reduction in root elongation and root lesions/rupturing.	Root elongation: 0.67 μM Ga in solution, no soil; lowest concentration. Rupturing: 1.7 μM Ga.	50% reduction in root elongation rate at 0.90 μM Ga.	Kopittke et al. (2009)
Rice	Reduction in relative growth rate, transpiration rate and water use efficiency	1.07 mg L^{-1} Ga in solution, no soil; lowest concentration.	-	Yu et al. (2015)
Chara corallina	Reduction in cell growth, and cell death.	20 mmol m^{-3} Ga petri dish treatment.	-	Reid et al. (1996)
Cucumber	Root growth inhibition.	80 μM Ga in solution, no soil.		Johnson & Burton (2007)
Wheat	Reduction in root elongation.	2.5 μM Ga in solution, no soil (only concentration used).	-	Snowden et al. (1995)

Table 2.11 Reported In toxicity symptoms and thresholds, in various plant species.

Species	Symptoms	Lowest concentration	Notable concentrations	Reference
-	Not specified; observed mainly in roots.	1-2 mg L^{-1}	-	Kabata-Pendias & Mukherjee (2007)
Onion	Reduction in root elongation and mitosis.	4 x 10^{-4}M $InCl_3$ (only concentration used).	Root elongation stopped after 6-9 hours.	Clarkson (1965)
Cowpea	Reduction in root elongation and root lesions/rupturing.	Root elongation: 0.36 μM In in solution, no soil; lowest concentration. Rupturing: 12 μM In.	50% reduction in root elongation rate at 0.72 μM In.	Kopittke et al. (2009)
Rice	Reduction in root length, shoot height, root and shoot biomass, and chlorophyll content.	0.04 mg L^{-1} In in solution, no soil; lowest concentration.	10% growth inhibition at 0.17 mg L^{-1}; 10% growth retardation at 15.4 μg $plant^{-1}$ shoot height, 10.6 for total biomass.	Syu et al. (2017)
Wheat	Reduction in root elongation.	2.5 μM In in solution, no soil (only concentration used).	-	Snowden et al. (1995)

2.2.3 Organic acid entry restriction

Entry of Ga and In can be reduced by organic acids in toxic environments, and there is evidence suggesting these elements may stimulate production. Multi-dentate complexation of phytotoxic species via acids such as citrate, oxalate and malate exuded from plant roots is a well-accepted strategy for ameliorating Al toxicity in acidic soils, rendering Al^{3+} non-physiologically active and/or incapable of entering the plant (Brunner & Sperisen, 2013; Kochian et al., 2004). Chang et al. (2017) reported a large increase in the expression of Al-activated citrate and malate transporting genes in *Arabidopsis thaliana* under toxic levels of Ga, doubling citrate root exudation in one treatment. Chang et al. (2017) and Ritchie & Raghupathi (2008) found that citrate (present in solution) was effective at detoxifying Ga, exhibiting behaviour very similar to Al. Many sources (Boros et al., 2014; Chang et al., 2017; Ritchie & Raghupathi, 2008; Salminen, n.d.b) have mentioned the capacity of both elements to be complexed by organic acids. Thus this process is highly likely to reduce Ga and In

uptake; directly-when concentration and acidity thresholds are crossed, or indirectly-when production is stimulated by Al toxicity at low soil pH.

2.2.4 Gallium substitution of iron

Gallium can replace Fe in many biological compounds, including ferric-chelate reductase (FCR) and phytosiderophores, which can induce Fe deficiencies. Ga^{3+} and Fe^{3+} have very similar ionic radii (0.620Å and 0.645Å), electronegativities (1.81 and 1.83) and ionic potentials (4.84 and 4.65, Table 2.1), causing similarities in chemical behaviour, notably binding strength, allowing substitution (Bernstein, 2005; Kelson et al., 2013). Though abundant, availability of Fe in many soils is low (Pestana et al., 2013), thus plants have evolved strategies to increase acquisition. One of the mechanisms employed by Strategy I plants (most species excluding the Gramineae family) is increased activity of FCR, an enzyme which releases Fe^{3+} from chelates for uptake (Johnson & Burton, 2007; Robinson et al., 1999). Strategy II plants release phytosiderophores, Fe^{3+} chelating compounds, and have a high affinity for their uptake (Römheld, 1987). Binding of Ga, to these compounds in particular, can greatly reduce uptake and cause deficiencies (Babula et al., 2008). Indium has a larger ionic radius, and is less likely to act as an Fe analogue (Boros et al., 2014). Essén et al. (2007) is one demonstration of Ga binding with siderophores. Syu et al. (2017) measured 36% and 57% reductions in root and shoot Fe concentrations respectively from addition of 15 mg L^{-1} Ga to a growing solution in rice plants.

Chapter 3

Materials and methods

3.1 Soil

A high fertility vegetable growing topsoil was used in this study. Soil was collected from 0-0.25m depth in Pukekohe, northern New Zealand (37°13'18.92''S 174°52'5.94''E), and dried, ground and sieved (Al Mamun et al., 2016). The soil was slightly acidic (pH H_2O 5.95), with a high cation exchange capacity (22.00 meq $100g^{-1}$), high base saturation (70.00%) and low organic carbon content (2.10%). Further chemical properties are present in Valentinuzzi et al. (2015).

Varying concentrations of lime were applied to soil used in the batch sorption experiments to alter the pH. Lime was lab-grade ($CaCO_3$, Thermo Fischer Scientific NZ Ltd.), and applied to soil in July 2014. Concentrations and pH values of the treatments are in Table A. 1.

3.2 Batch sorption experiments

Stock solutions containing 1000 mg L^{-1} Ga or In, used throughout the batch sorption experiments, were prepared by addition of 367 mg gallium nitrate ($Ga(NO_3)_3$) or 262 mg indium nitrate ($In(NO_3)_3$) to 100 mL volumetric flasks made to volume with DI water. Calcium nitrate ($Ca(NO_3)_2$) extractant solution, 0.05 M, was prepared by dissolution of 11.80 g $Ca(NO_3)_2$ in 1 L DI water. Some of the extractant solution was then spiked by Ga or In, by replacement of 10 mL $Ca(NO_3)_2$ with 10 mL of stock solution, producing 1 L of 10 mg L^{-1} Ga or $In(NO_3)_3$/0.05 M $Ca(NO_3)_2$.

The standard procedure involved 30 mL Ga or $In(NO_3)_3$/0.05 M $Ca(NO_3)_2$ dispensed into a centrifuge tube with 5 g T1 soil, 2 hours in an end-over-end shaker, 10 minutes in a Kubota centrifuge at 3,000 rpm, and filtering into 30 mL pottles via Whatman 51 filter papers and funnels. Extracts were stored in a fridge or freezer until chemical analysis.

Initially, 30 mL $Ga(NO_3)_3$/0.05 M $Ca(NO_3)_2$ and $In(NO_3)_3$/0.05 M $Ca(NO_3)_2$ were each added to 18 tubes, 15 containing 5 g soil. Three were on the end-over-end shaker for 30, 60, 120 and 240 minute durations, with six tubes, including those without soil, remaining for 480 minutes. These tests proved that sorption was relatively stable after 120 minutes (Figure A. 1), thus was used as a control for the other treatments.

To test the effect of pH on partitioning, 5 g of T2, T3, T4 and T7 soil were added to 6 tubes, differing in the concentration of lime applied (Table A. 1). Half were supplied with 30 mL Ga or $In(NO_3)_3$/0.05

M $Ca(NO_3)_2$, and half with pure $Ca(NO_3)_2$. Another three tubes were supplied with Ga/In and pure extractant solution.

To test the effect of contaminant concentration on partitioning, calcium nitrate extractant solutions containing 1, 3, 30 or 100 mg L^{-1} Ga or In were prepared. The 100 mg L^{-1} solution was formed by addition of 25 mL Ga or In stock to a 250 mL volumetric flask and levelling with pure $Ca(NO_3)_2$. Then 2.5 mL of this solution was pipetted and levelled into another flask to gain a 1 mg L^{-1} solution. The 30 mg L^{-1} solution was produced from 7.5 mL stock in 242.5 mL $Ca(NO_3)_2$, and 3 mg L^{-1} from 25 mL of the 30 mg L^{-1} solution into a fourth flask. Solutions were dispensed; 30 mL each in six tubes; three containing 5 g T1 soil and three without.

3.3 Plant uptake experiments

Solutions were prepared by dissolution of 14.67 g $Ga(NO_3)_3$ and 262 mg $In(NO_3)_3$ in 100 mL DI water, transferred to spray bottles, and evenly incorporated in 2 kg of soil. Thus the concentration increased by 2000 mg kg^{-1} Ga or 200 mg kg^{-1} In. Then 1 kg was set aside, and 1 kg of fresh soil evenly incorporated; this process was repeated until ≥1 kg of soil contained 2000, 1000, 500, 250, 125, 62.5, 31.25 and 15.125 mg kg^{-1} added Ga, and 200, 100, 50, 25, 12.5, 6.25, 3.125 and 1.5125 mg kg^{-1} In. Soil was then partitioned, with 250 g of each soil treatment in four filter paper-lined pots with saucers, in addition to four without Ga or In added.

Pots were transferred to a growth chamber, and sprayed overhead daily until water had emerged from the bottom of the pot, for three days. On the fourth day, the soil surface remained damp thus the saucer was filled with water for four days.

One week after soil spiking, surfaces were roughened and 0.10-0.12 g perennial ryegrass seed (*Lolium perenne*, var. Arrow) was evenly sprinkled over top.

Saucers were filled with water daily, approximately 20-28 hours apart, for 6 weeks. A sheet of clear plastic placed overhead was removed after 6 days when all pots had visibly germinated. 40 mL of 10,000 mg L^{-1} urea was applied to each pot 4 weeks after sowing, to ameliorate the nitrogen deficiency symptoms (reduced growth rates and yellower leaves) observed in pots with <500 mg kg^{-1} Ga or In NO_3^- salt.

After 6 weeks, foliage was harvested to approximately 1.5-2 cm above the surface, rinsed with DI water, and placed in separate paper towels and bags in a drying oven for 7 days. Samples were weighed and ground to a fine powder with a small portable grinding-machine.

3.4 Chemical analysis

Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the chemical composition in both sections of this study. Gallium and In batch sorption extracts had 1.41 ± 1.98 mL and 2.78 ± 0.07 mL of concentrated nitric acid (HNO_3) respectively applied prior to measurement, producing a dilution factor of 5. Plant samples underwent microwave digestion (0.1996-0.2023 g with 2 mL 69% HNO_3, 2 mL 30% H_2O_2, and made to 10 mL volume), before 1 mL was diluted with 4 mL strong HNO_3, also producing a dilution factor of 5, prior to ICP-MS analysis. Ga and In were measured, in addition to B, Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Zr, Nb, Mo, Cd, Sb, Ta, W, Re, Pb, Rh.

3.5 Data analysis

3.5.1 Batch sorption

Solution and soil matrix concentrations were extracted to calculate the distribution coefficient; equations in Appendix A.1.1. Correction factors were applied, to account for the mass retained in filter paper and other equipment.

3.5.2 Plant uptake

Shoot biomass concentrations were calculated (Equation A. 7), and negative values (lower than ICP-MS blank average) were removed from analysis.

3.5.3 Presentation

Correlation analysis, summary statistics and graphs were produced in Excel. Correlations utilized data from control pots and soil spiked with the respective elements; r=0.329 was the significance threshold (Biology For Life, n.d.). Error bars on graphs consisted of the treatment standard deviations. One-way ANOVA (analysis of variance) and post-hoc Fisher's Unprotected LSD (least significant differences) tests were completed in Genstat 16th edition.

3.6 Modelling

Visual MINTEQ 3.1 is a numerical equilibrium speciation model. It utilizes equilibrium and solubility constants for chemical reactions between present elements, to estimate the concentrations of aqueous and precipitated species in an aqueous system (Gustafsson, 2016).

Modelling was completed to estimate the relative abundances of the hydroxide species present, in the $Ca(NO_3)_2$ extractant solution with 10 mg L^{-1} Ga or In added. Species inputted and parameters are listed on Table A. 2.

Chapter 4

Results

4.1 Retention of gallium and indium to the soil matrix

Most of the added Ga and In was retained by the soil matrix. When averaged across a range of concentrations with the standard procedure (T1 soil and 120 minutes shaking time), In had a much higher distribution coefficient at 2021.4, compared to Ga at just 408.13 (Figure 4.1).

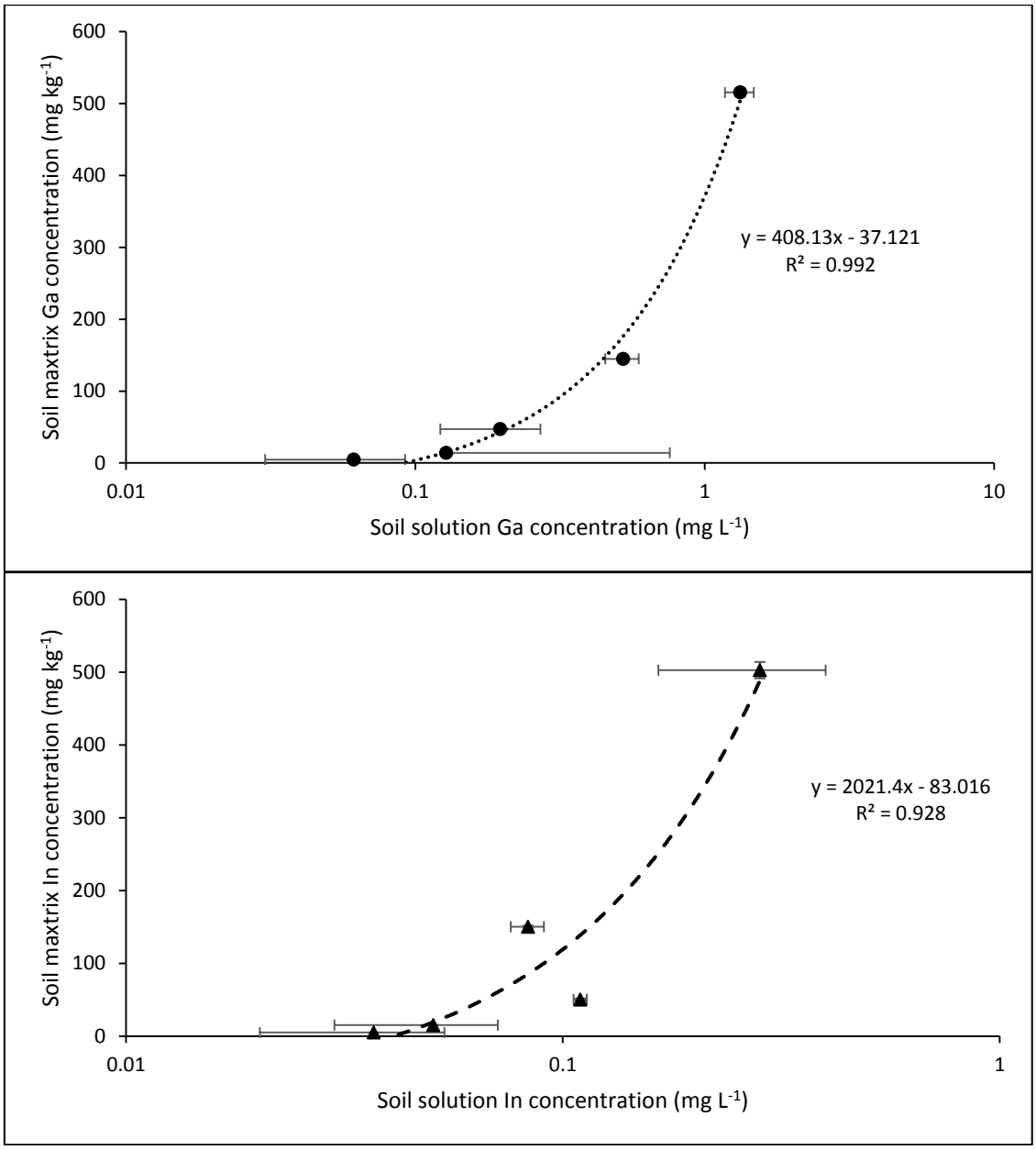

Figure 4.1 Partitioning of Ga and In between the soil matrix and soil solution. Mean values of each treatment presented (*n*=3), differing in the concentration of Ga or In added. Error bars denote standard deviation of soil solution and matrix for each concentration category.

4.1.1 Factors affecting rentention

4.1.1.1 Solution pH

Retention of both elements decreased as the pH of the solution increased (Figure 4.2). K_d of Ga decreased from 689 at approximately pH 5.54, to 265 at 7.14. Indium decreased from 1266 to 458 across the same scale, and though the trendline was of similar shape K_d was consistently 73-153% higher than Ga.

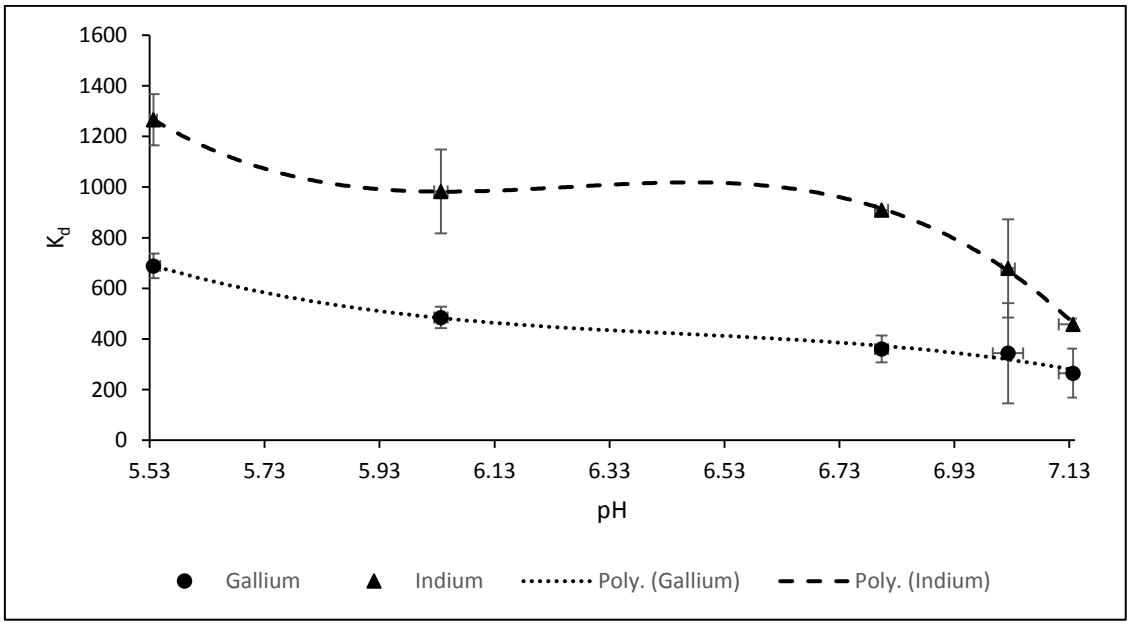

Figure 4.2 Effect of extractant solution pH on K_d of Ga and In. Mean values of each treatment presented. Error bars denote standard deviation of K_d and pH categories. 3 replicates, except *n*=2 Ga K_d pH 6.04, *n*=5 In K_d pH 7.02, *n*=1 In K_d pH 6.80 (experimental error).

4.1.1.2 Concentration added

Retention of Ga and In logarithmically increased with the concentration added to the extracting solution (Figure 4.3). Gallium's distribution coefficient rose from 88 to 392, and In 163 to 3187 over the range tested in this study. Both 10 and 30 mg L^{-1} (458 and 1812 K_d) In treatments were not consistent with the trendline, but the other three treatments fit the Ga analogous curve well.

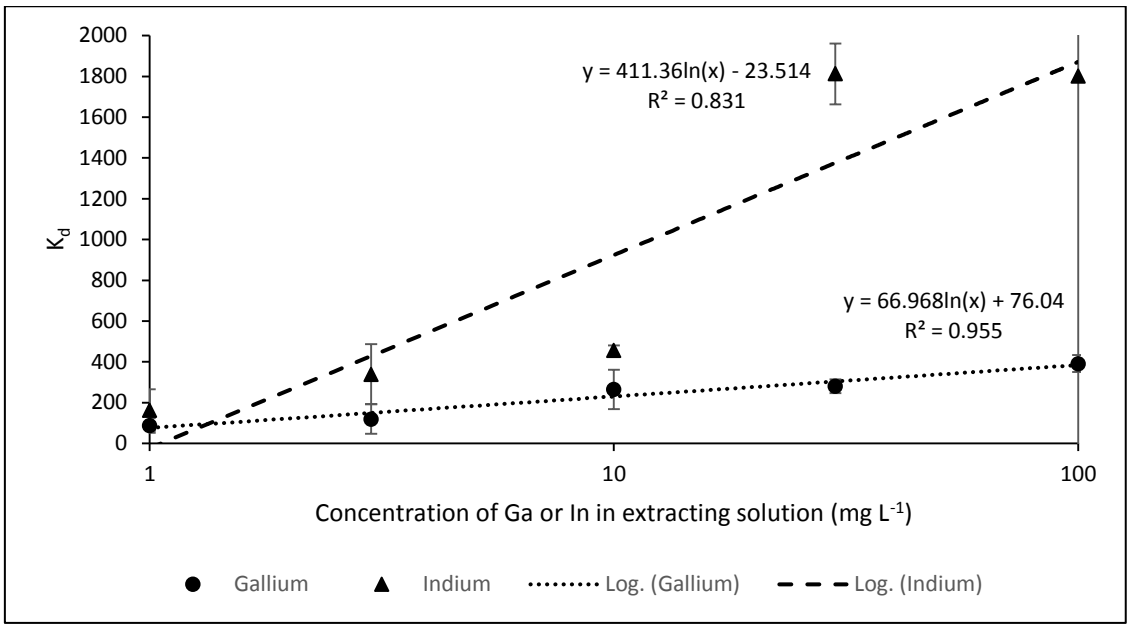

Figure 4.3 Effect of extractant solution Ga and In concentration on K_d Mean values of each treatment presented (*n*=3), differing in the concentration of Ga or In added. Error bars denote standard deviation of K_d for each concentration category.

4.2 Gallium and indium hydrolysis modelling data

Visual MINTEQ 3.1 data predicted that Ga and In ions would hydrolyse in solution, with variation in aqueous speciation and degree of Ga precipitation across the pH range tested. Figure 4.4 and Figure 4.5 demonstrate differences in the relative concentrations of Ga and In mononuclear hydroxide species in identical solutions; Ga hydrolysis was predicted to occur at a lower pH range than In, with greater prominence of mono and divalent cations. Aqueous $Ga(OH)_3$ was absent from the model, though precipitation of both forms ($Ga(OH)_3$ and GaOOH) was modelled to peak at pH 5 (Figure 4.6). Sufficient In precipitation data was unable to be extracted. $Ga(OH)_4^-$ was predicted to be the predominant species in all extractant solutions in this study, accounting for >93% of aqueous Ga, though monovalent cation dominance increased with acidity (Table 4.1). Precipitation steadily decreased as pH increased. Indium was predominantly as $In(OH)_{3\,(aq)}$, though monovalent $In(OH)_2^+$ was modelled to also be particularly abundant in the T1 soil treatment (Table 4.2). Extremely little (<1%) of the anion was predicted to be present.

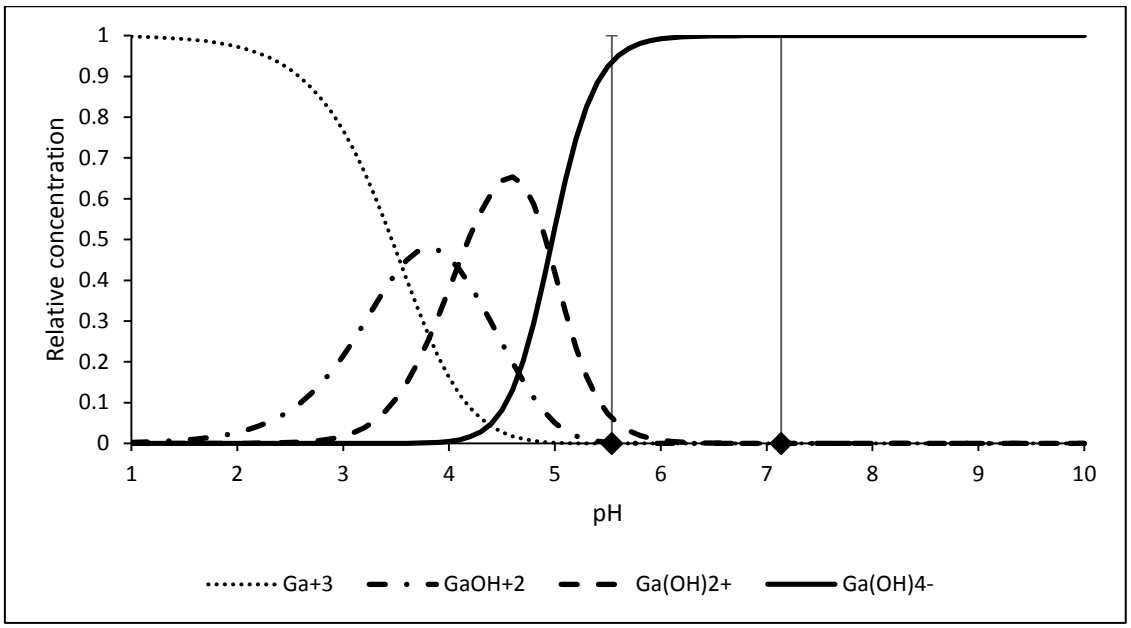

Figure 4.4 Approximate relative concentrations of aqueous mononuclear Ga hydroxyl species in extractant solution, generated from Visual MINTEQ 3.1. ◆ denotes the lower and upper limits of the pH range tested in batch sorption experiments. Concentrations are relative to the total concentration of mononuclear hydroxyl species.

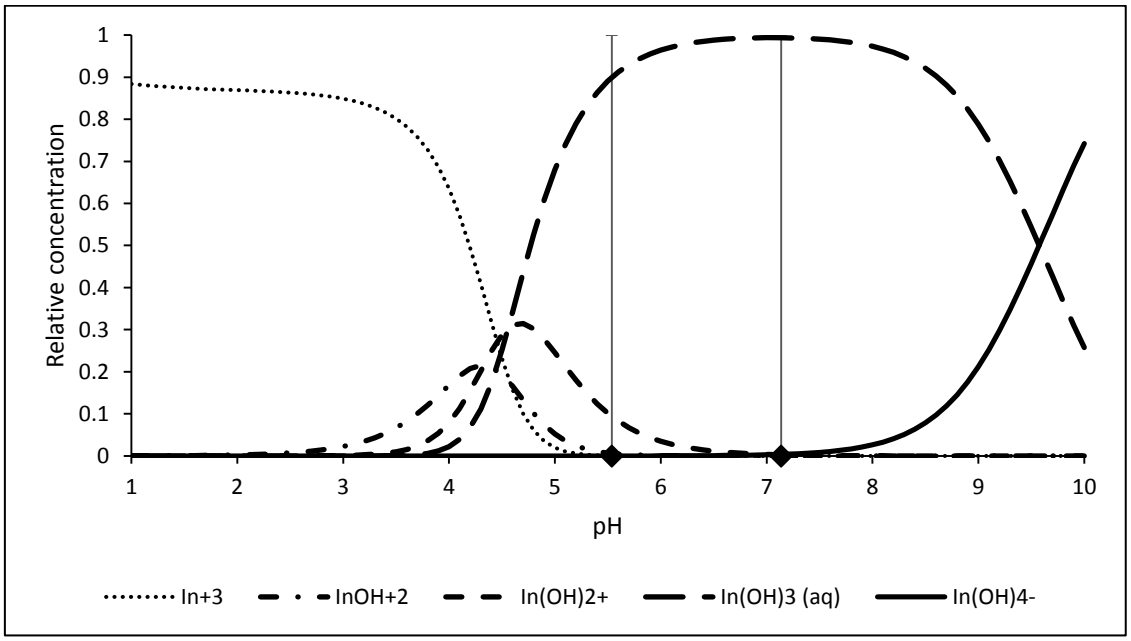

Figure 4.5 Approximate relative concentrations of aqueous mononuclear In hydroxyl species in extractant solution, generated from Visual MINTEQ 3.1. ◆ denotes the lower and upper limits of the pH range tested in batch sorption experiments. Concentrations are relative to the maximum total concentration of mononuclear hydroxyl species.

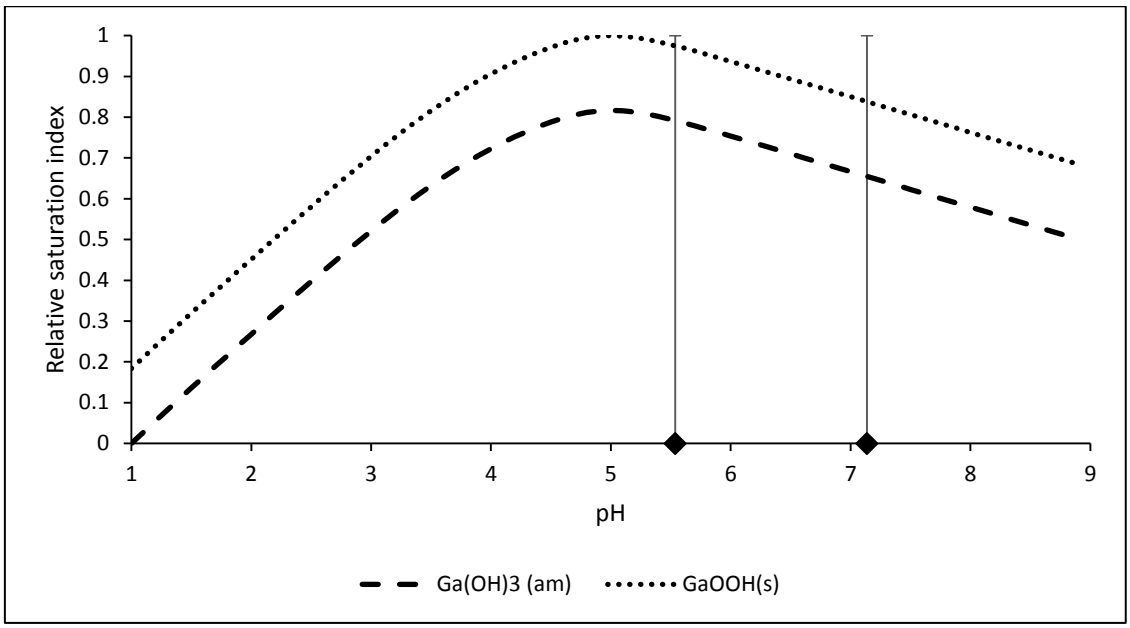

Figure 4.6 Approximate relative saturation index of Ga hydroxyl precipitates in extractant solution, generated from Visual MINTEQ 3.1. ◆ denotes the lower and upper limits of the pH range tested in batch sorption experiments. Saturation index is relative to the maximum of GaOOH when all generated saturation index values were raised to ≥0 (6.999 added).

Table 4.1 Approximate relative concentrations of aqueous mononuclear Ga hydroxyl species and saturation index of precipitates, in extractant solution at pH tested, generated from Visual MINTEQ 3.1. Saturation index = log IAP (ion activity product) - log Ks (solubility constant).

Soil type	pH	Aqueous species (% of total concentration)				Precipitated species (saturation index)	
		Ga^{3+}	$Ga(OH)^{2+}$	$Ga(OH)_2^{+}$	$Ga(OH)_4^{-}$	$Ga(OH)_3$ (am)	GaOOH(s)
T1	5.54	<0.001	0.218	6.223	93.558	2.07	4.173
T2	6.04	<0.007	<0.007	0.661	99.332	1.596	3.699
T3	6.80	<0.001	<0.001	0.019	99.98	0.833	2.935
T4	7.02	<0.007	<0.007	<0.007	99.993	0.613	2.715
T7	5.54	<0.004	<0.004	<0.004	99.996	0.499	2.601

Table 4.2 Approximate relative concentrations of aqueous mononuclear In hydroxyl species, in extractant solution at pH tested, generated from Visual MINTEQ 3.1.

Soil type	pH	Aqueous species (% of total concentration)				
		In^{3+}	$In(OH)^{2+}$	$In(OH)_2^{+}$	$In(OH)_3$ (aq)	$In(OH)_4^{-}$
T1	5.54	0.064	0.579	9.419	89.921	<0.017
T2	6.04	0.029	0.062	3.203	96.704	<0.002
T3	6.80	<0.002	<0.002	0.563	99.264	0.171
T4	7.02	<0.001	<0.001	0.339	99.376	0.284
T7	7.14	<0.001	<0.001	0.261	99.369	0.369

4.3 Physiological uptake of gallium and indium by ryegrass

4.3.1 Concentration of gallium and indium in shoot biomass

Low concentrations of Ga and In were present in ryegrass shoots, logarithmically increasing with soil concentrations (Figure 4.7). Gallium uptake increased consistently from 0.06 to 11.57 mg kg^{-1} DM as soil concentrations increased to 2000 mg kg^{-1} (Figure A. 5). Indium concentrations also increased with soil addition above 25 mg kg^{-1}, but plateaued at 0.015 with 100 mg In kg^{-1} soil (Figure A. 6). Uptake by Ga was much higher than In; the size of the difference increased with concentration, from 36% at 1.5625 mg kg^{-1} to 23,372% at 2000 mg kg^{-1}.

Control treatments (0.11 mg kg^{-1} DM Ga and 0.0058 mg kg^{-1} DM In) were assumed indicative of the division of treatments above and below the detection limit, as shoot concentrations consistently increased with soil concentrations above these thresholds. Thus they were used as an approximation of the detection limit in this study. The 15.625 mg kg^{-1} Ga and 1.5625, 3.125, 6.25, 12.5, and 25 mg kg^{-1} In treatments were below the detection limit.

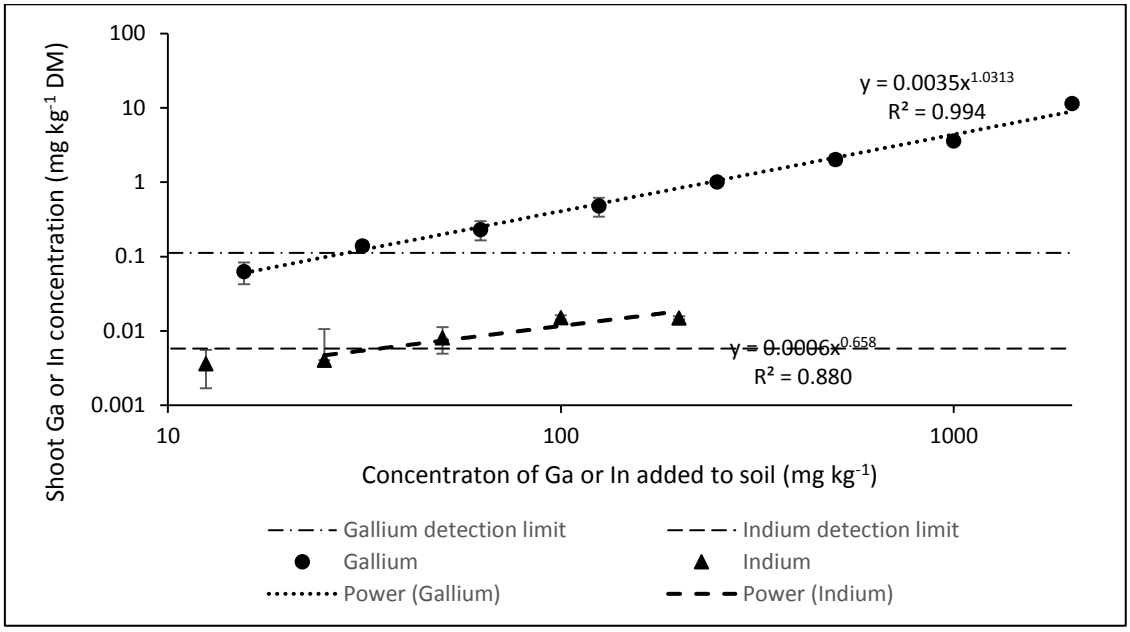

Figure 4.7 Effect of the concentration of Ga and In added to soil on ryegrass shoot concentrations. Mean values of each treatment presented (*n*=4). Error bars denote standard deviation of biomass concentration for each category. Detection limit assumed equal to control, 0.11 mg kg^{-1} DM Ga and 0.0058 mg kg^{-1} DM In, thus 0 mg kg^{-1} Ga and 0-6.25 mg kg^{-1} In treatments not shown.

4.3.1.1 Uptake relative to soil application

Little of the total mass of Ga and In applied was present in the shoot biomass. Gallium uptake increased linearly from 0.0027% to 0.013% (Figure 4.8), while In decreased exponentially from 0.0021% to 0.000039%. Uptake of In was much lower, even when the effect of increased soil

retention was removed, though is not directly comparable due to different trendline curves (Figure 4.9).

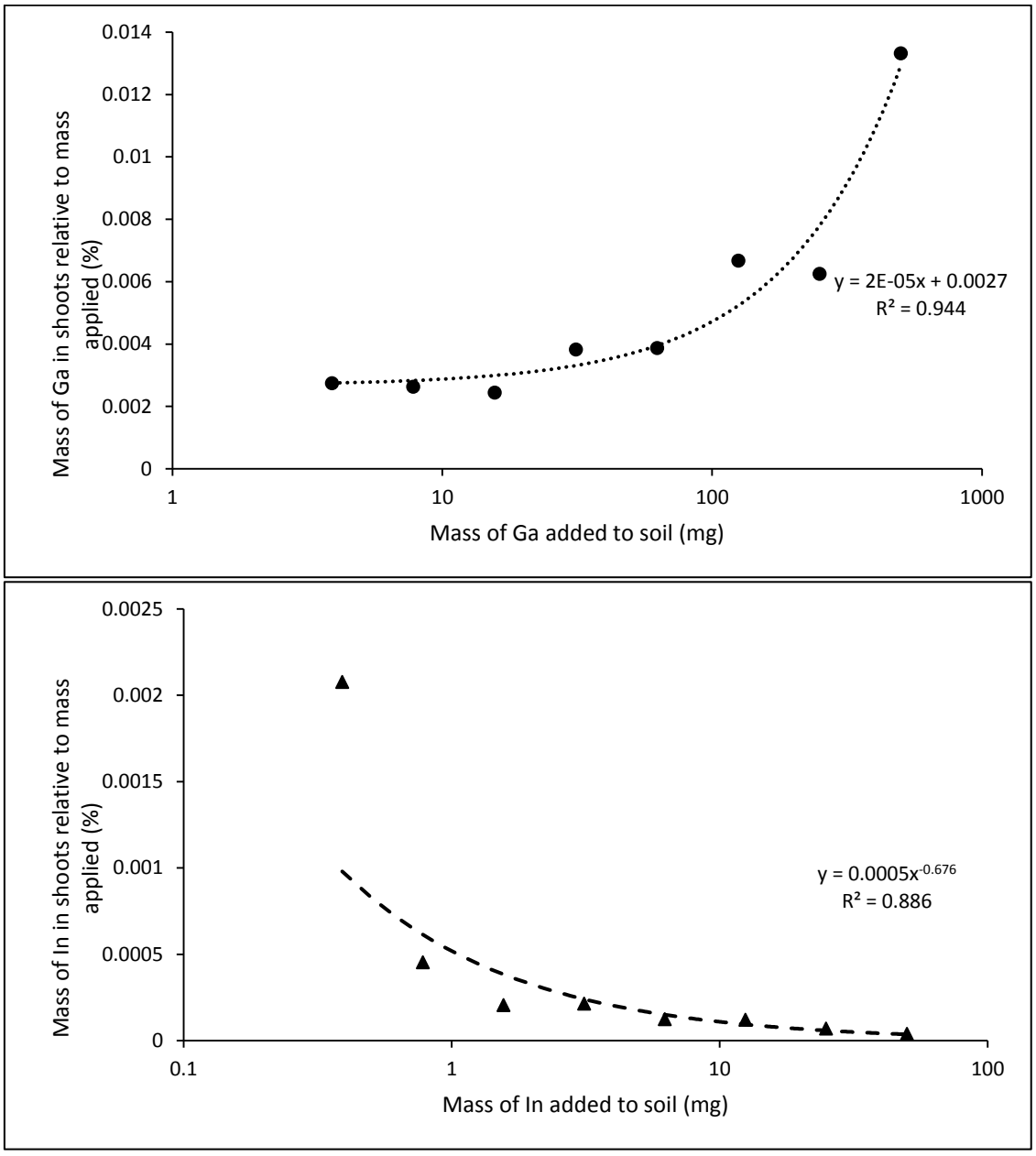

Figure 4.8 Effect of the mass of Ga and In added to soil on the mass in harvested ryegrass shoot biomass. Mean values of each treatment presented (*n*=4).

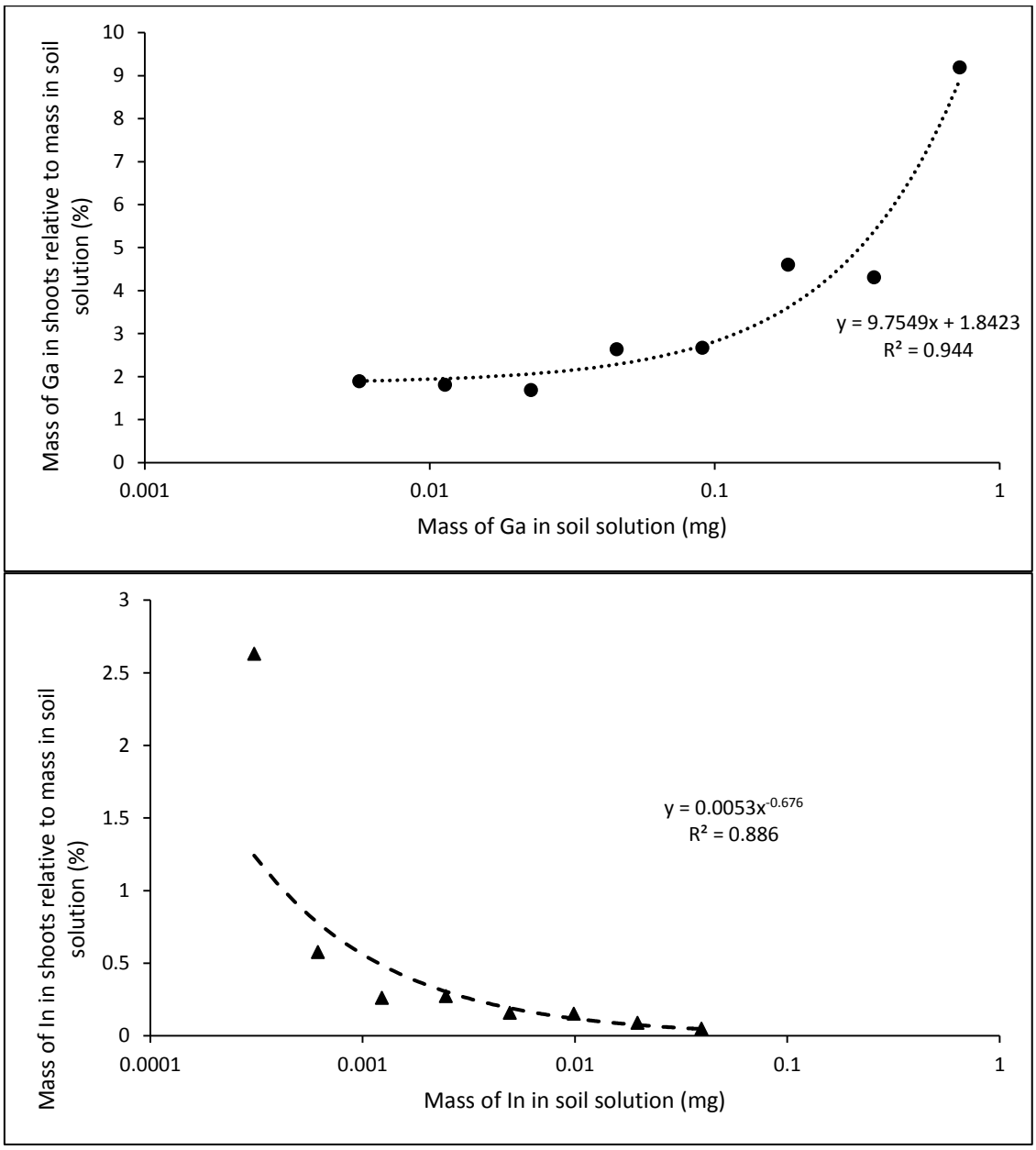

Figure 4.9 Effect of the predicted soil solution mass of Ga and In added to soil on the mass in harvested ryegrass shoot biomass (*n*=4). Mean values of each treatment presented.

4.3.2 Effect of gallium and indium on elemental uptake

4.3.2.1 Correlations with other elements

The threshold of significance ($p \leq 0.05$) for relationships in data collected was $r \geq 0.329$ (34 degrees of freedom, significance table from Biology For Life (n.d.)). Mg, Ca, Zn, Cd, Mn, Na and Ni formed strong positive correlations with the concentration of Ga in ryegrass shoots, and K, Si, Mo, Fe, As, Ge, W, Co and Cu were negatively correlated (Table 4.3). Almost 80% of the variation in Mg could be explained by the degree of Ga uptake. Indium showed positive correlations with Cd, Mo and B, but with the exception of Cd, In formed much weaker relationships than Ga and no significant negative relationships were found (Table 4.4).

Table 4.3 Significant correlations between Ga and other elements in ryegrass shoots. p≤0.05; r≥0.329 significance threshold. 36 samples, 9 treatments.

Positive relationship	
Element	Correlation coefficient
Mg	0.893
Ca	0.801
Zn	0.711
Cd	0.691
Mn	0.690
Na	0.683
Ni	0.338
Negative relationship	
Element	Correlation coefficient
Cu	-0.340
Co	-0.480
W	-0.552
Ge	-0.590
As	-0.598
Fe	-0.643
Mo	-0.664
Si	-0.754
K	-0.833

Table 4.4 Significant correlations between In and other elements in ryegrass shoots. p≤0.05; r≥0.329 significance threshold. 36 samples, 9 treatments.

Positive relationship	
Element	Correlation coefficient
Cd	0.710
Mo	0.352
B	0.344

4.3.2.2 Interaction between gallium and indium

There was not a significant relationship between Ga and In shoot biomass concentrations in soil spiked with the opposing element; r correlation coefficients were 0.087 and 0.137 in Ga and In spiked soil respectively, below the 0.329 significance threshold (Biology For Life, n.d.).

4.3.2.3 Correlation with iron

Concentrations of Fe in ryegrass shoot biomass decreased with uptake of Ga, from 90.6 to 37.5 mg kg^{-1} as Ga increased from 0.11 to 11.5 mg kg^{-1} (Figure 4.10). No significant relationship was

observed with In (Figure 4.11). One-way ANOVA produced p values of <0.001 and 0.024 respectively for the two sets of data.

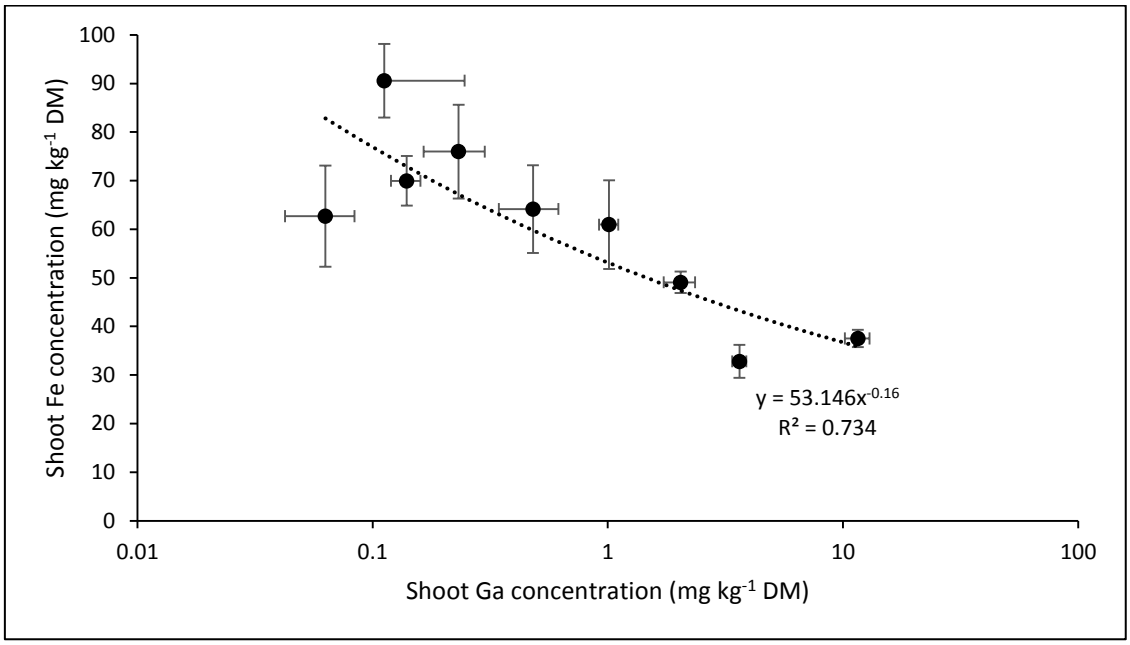

Figure 4.10 Relationship between the concentration of Ga and Fe in ryegrass shoot biomass. Mean values of each treatment presented (*n*=4). Error bars denote standard deviation of biomass concentration for each Ga concentration category and controls.

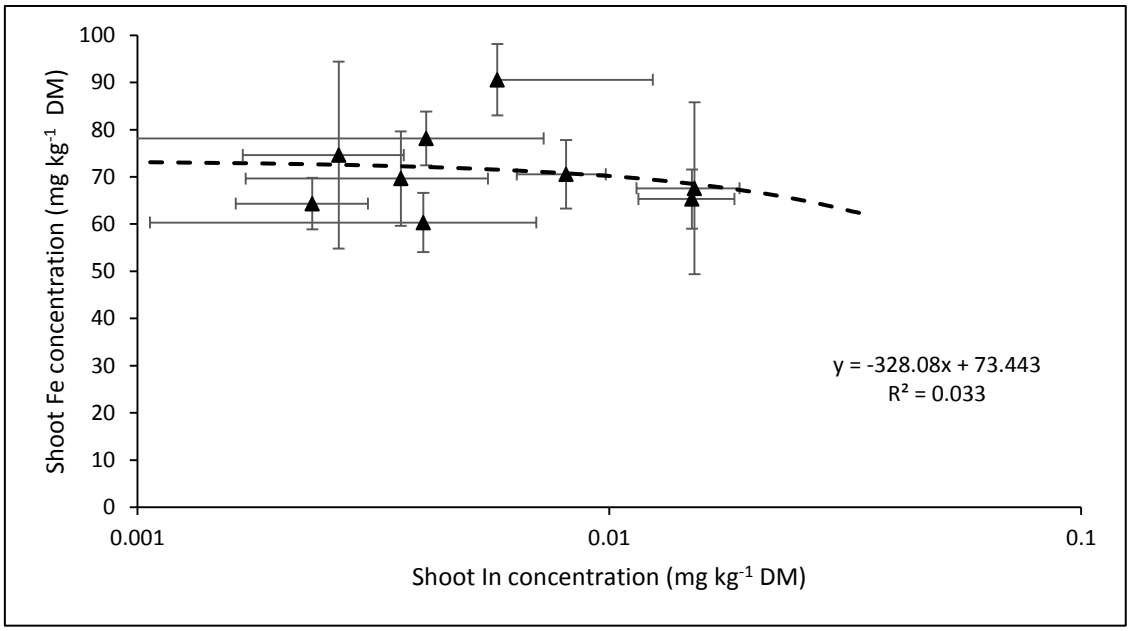

Figure 4.11 Relationship between the concentration of In and Fe in ryegrass shoot biomass. Mean values of each treatment presented (*n*=4). Error bars denote standard deviation of biomass concentration for each In concentration category and controls.

Chapter 5

Discussion

5.1 Partitioning of gallium and indium between the solid and solution phases in soil

Gallium and In were strongly retained by soil colloids. Approximately 400 and 2000 times more Ga and In were retained by the matrix versus present in the extractable fraction (Figure 4.1), and across a range of treatments mean K_d never fell below 82 (3 mg kg^{-1} Ga), peaking at 3187 (100 mg kg^{-1} In) (Table A. 3). Due to the small size of the fraction remaining in solution, both elements are thus expected to have low mobility and bioavailability. This trend is consistent with findings from all applicable partitioning studies (measured the concentration of aqueous relative to solid-phase Ga or In), such as Boughriet et al. (2007), Sheppard et al. (2009) and Tyler & Olsson (2001), listed in Table 2.2, Table 2.3, Table 2.4 and Table 2.5. Despite presenting insufficient data for calculation of K_d, in another soil-spiking study Hou et al. (2005) found that after 18 months, ≤8% of In applied to the surface of Cambisol, Fluvisol and Regosol soil tubes in-field was exchangeable. 62-95% remained in the uppermost 2 cm.

5.1.1 Factors affecting the degree of partitioning

5.1.1.1 Time after application

Retention of both elements was rapid, with sorption expected to slowly continue beyond the range measured (Figure A. 1). The shaking time gradient was completed to validate that sorption was relatively stable after 120 minutes, thus was a suitable parameter for the other tests. However, it was valuable at demonstrating that sorption increased with time. Increased incorporation with associated exposure to superficial sorption sites is the hypothesised mechanism. The relationship between sorption time and K_d was strongest for Ga (R^2 0.976 versus 0.038), but due to similarities in chemical properties and soil behaviour (Chapter 2.1) In is expected to follow a similar trend, with error the believed cause of poor fit. The treatment range only extended to 480 minutes, thus longer experimentation is required to identify when sorption peaks or increments are statistically insignificant-though poorly feasible with the methodology used.

5.1.1.2 Soil solution pH

5.1.1.2.1 Prediction of aqueous species and precipitation

Data from Visual MINTEQ 3.1 predicts that $Ga(OH)_4^-$ and $In(OH)_3$ were the dominant aqueous speciation in this study. Figure 4.4 and Figure 4.5 show the effect of increasing pH on the degree of hydrolysis, with the differences in ranges of transformation (pH 2-6 Ga, 3->10 In) consistent with

earlier theory that ionic Ga is more acidic than In due to its smaller ionic radius (Chapter 2.1.2.1). Table 4.1 and Table 4.2 show that $Ga(OH)_4^-$ and $In(OH)_3$ dominated in the 5.54-7.14 pH range in this study, accounting for 93.6->99.9% and 89.9-99.4% of aqueous Ga and In respectively.

The model is not completely reflective of the complex soil system, thus should only be used as a qualitative guide to aid in understanding the processes contributing to the mobility characteristics. Soil contains many behaviour-defining species other than $Ca(NO_3)_2$, $Ga/In(NO_3)_3$, H_2O and CO_2 inputted (Table A. 2), along with colloids and organic material, though due to extensive variation in form and concentration it is infeasible to measure nor guess all other constituents for use in the model. A few common examples include aqueous complexation of In with Cl (producing $InCl^{2+}$, $InCl_2^+$ and $InOHCl^+$), availability-limiting Ga F complexation, and acidity-exacerbated organic acid sorption (Chang et al., 2017; Kabata-Pendias & Mukherjee, 2007; Wood & Samson, 2006; Chapter 2.2.3). Staff et al. (2010) simulated complexation of all aqueous Ga at pH 3-5 by EDTA (ethylenediaminetetraacetic acid) and citrate when present. Figure 25 in Wood & Samson (2006) demonstrated the complexity of an In solubility model arising from the addition of just two extra elements, S and Cl. In this study, only the hydroxyl species were modelled. Water is abundant, and guaranteed to influence behaviour. Complexes with other elements are substrate-concentration limited, in aqueous systems (Wood & Samson, 2006), with sorption further limiting availability in soil. Another factor contributing to inaccuracy is temperature; the degree of hydrolysis at a particular pH value increases with heat. Though temperature can be inputted to the model, it was not measured during experimentation and varied throughout and between days, thus the 20°C inputted was inaccurate. However, over relatively small ranges the effect is expected to be relatively small; Wood & Samson (2006) modelled that a 225°C increase was required for $In(OH)_4^-$ abundance to rise from 0% to 50% at pH 7.

Unexplained differences between this model and literature data further emphasise its recommendation to only be used as a guide. Although the solubility of Ga (particularly $Ga(OH)_3$) is reportedly extremely low (Bernstien, 1998), a small aqueous fraction should be present on Figure 4.4 (the hydrolysis graph). Wood and Samson (2006) calculated that $Ga(OH)_{3\,(aq)}$ composed approximately 10% of aqueous Ga at pH 4.4, and Kopittke et al. (2009) modelled 10% at pH 3.7 and 40% at pH 4.3, using PhreeqcI. Temperature could be partially responsible-a 5°C lower value was inputted to the model-but is likely to only cause a slight reduction, inferred from the graphs in Wood and Samson (2006). Differences were also observed among relative fractions of cationic Ga species. Wood & Samson (2006) showed that $GaOH^{2+}$ was a much more dominant species than $Ga(OH)_2^+$ at low temperatures, the opposite of the suggestion by Minteq, with modelled data produced by Staff et al. (2010) showing further variation. Theoretically, when only hydroxide species are considered,

speciation dominance should be similar. The type of modelling software used (age, structure, data) is likely predominantly responsible.

The soil matrix-associated fraction could not be separated into adsorption and precipitation, limiting understanding of the behaviour of these elements. Precipitated and strongly adsorbed Ga and In are both not likely to be bioavailable, thus not extracted by $Ca(NO_3)_2$ in the methodology used. Unfortunately, Minteq modelling did not provide sufficient insight; Figure 4.6 shows that Ga precipitation decreases above a peak at pH 5.0, but data could not be extracted comparing the concentration relative to the aqueous hydroxyl species available for potential sorption, nor the effect of increasing concentration on the fraction precipitated. Of the pH range tested $In(OH)_3$ was reportedly the dominant species, but precipitation data was not extracted. Literature indicates that precipitation is extremely frequent-low solubility thresholds have been reported, such as 0.069723 mg Ga L^{-1} at pH 7.4 and 25^{o}C from Berstein (1998), and 2-15 x10^{-6} mg In L^{-1} in European streams from Ladenberger et al. (2015)-but does not quantify it relative to sorption processes, which are also believed to remove notable quantities of ions from solution. Thus understanding of the processes causing the immobility of Ga and In is limited.

Sequential extraction procedures are a possibility to provide some clarity in future research, but are incapable of fully separating sorption and precipitation. This process quantifies the partitioning of elements between 4-5 fractions; exchangeable and/or carbonate (soluble and bioavailable), reducible (oxide forms), oxidisable (sulphides and organic matter), and residual (silicates and resistant oxidisable material). It appears relatively frequently in literature, predominantly based of the methodology developed by Tessier et al. (1979) using extractants of various strengths and chemical properties. Połedniok (2012) is a Ga example, and Waterlot et al. (2013), Boughriet et al. (2007) and Hou et al. (2005) measured In. The fraction sorbed to organic material, sulphide and residual/resistant minerals can be separated from precipitation. However, the reducible fraction cannot be partitioned into oxide precipitation versus Mn and Fe oxides/hydroxides sorption, thus the key limitation is still present. In French soils contaminated from Pb and Zn smelters, Boughriet et al. (2007) measured 59% reducible In, and Waterlot et al. (2013) 52.1-90.1% in 11 garden with >75% in 11 lawn samples. Both authors believed In oxide compounds to predominate this fraction, but were unable to quantify the extent. Total and extractable Ga followed a similar distribution pattern and was strongly associated with Fe within a Haplic Pozdol soil profile, in data collected by Tyler (2004b), which shows that precipitation likely does not compose the entirety of that fraction.

5.1.1.2.2 Variation in retention with pH

Distribution coefficients of Ga and In decreased with increasing with pH, though responsible mechanisms can only be speculated. Figure 4.2 shows that has pH increases, retention by the soil

matrix decreases, causing these elements become more mobile in the system and susceptible for plant uptake. Adsorption and precipitation processes independently vary with pH. Gallium precipitation decreases linearly above and below a peak at approximately 4.3-5.2 (Figure 4.6, Berstein (1998), Wood & Samson (2006)), and In outside the 4.5-9 pH range (Wood & Samson, 2006). Gallium and In soil sorption specifics remain unclear (Chapter 2.1.2.2.1) but cation adsorption is widely accepted to increase with pH, with anion adsorption decreasing. Models provide sufficient predictions of the relative abundance of various species, but cannot separate the two key processes nor indicate the species involved in each process (for example, the polyvalent cation fraction is more susceptible to sorption than monovalent cations).

Hypotheses were formed involving partitioning between the tri and tetrahydroxide species, which could potentially partially explain the slope of the pH distribution coefficient graph (Figure 4.2). K_d of In decreased particularly rapidly from pH 6.80 to 7.14 (910 to 458). Within that range, the fraction of $In(OH)_3$ was modelled to remain relatively similar (99.264-99.376%, Table 4.2), but $In(OH)_2^+$ decreased from 0.563 to 0.261%, and $In(OH)_4^-$ increased from 0.171 to 0.369%. Thus it is interpreted that the anionic species was lesser retained by the matrix. This is consistent with Ga data; retention was continually lower across the pH gradient (K_d ≥193 less), which can be attributed to the continually smaller cation fraction. When the distribution coefficient decreased 26% pH 6.80-7.14, $Ga(OH)_4^-$ was modelled to increase from 99.98% to 99.996%. No literature sources were found to compare cationic and anionic Ga and In sorption and thus verify this theory.

The polynomial trendline in Figure 4.2 is not unexpected considering the curvilinear nature of the hydrolysis models, but poses difficulties for extrapolation beyond the pH range used in this study. pH 5.54-7.14 is common across most agricultural soils, as optimum growth for many species occurs within this range (DeSutter & Godsey, 2010; McLaren & Cameron, 1996), but can differ on unimproved soils, which are more susceptible for disposal of waste due to their decreased growth potential, or be altered by contamination. Up to pH 8.2 was measured on contaminated soils containing 0.08-1.56 mg kg^{-1} In from previous Pb and Zn smelters (Waterlot et al., 2013). Oxidisation of 9 year old Pb-Zn tailings caused the pH to drop to 4.93, recorded by Wong et al. (1998). Thus data produced cannot be used to predict the relative mobility at extreme soil pHs.

Contrary to this data, other literature found that the distribution coefficient of Ga increased within a similar pH range, thus further analysis is required to reach a consensus. Aqueous Ga decreased and calculated K_d rose from approximately 0.06 µg L^{-1} and 333,333 respectively, to 0.015 µg L^{-1} and 1,333,333 as the pH increased from 5.37 to 7.25, in a study by Tyler & Olsson (2001) which modified the pH of natural soil (uncontaminated and uncultivated, unlike the heavily cultivated horticultural soil in this study) via $CaCO_3$ additions. However, the curve of the trendline suggested solution

concentrations and thus mobility could increase if the range was expanded, and was poorly fitting. The authors offered little explanation of mechanisms, but mentioned the strong relationship between Ga and Al; Al and Fe solubility decreased rapidly, which could contribute through increased quantities of sorption sites. Watmough (2008) found that the distribution coefficient of Ga logarithmically increased with pH, from approximately 10,000 at pH 4 to close to 100,000 at pH 7. Though opposite to the findings in this study, their linear trendline was also a poor fit (R^2 = 0.44), implying that the curvilinear partitioning of ionic species and precipitates also influenced data. pH was strongly statistically explanatory of K_d data from clayey and peat Swedish soils, but Sohlenius et al. (2013) hypothesised that the reduction in K_d with pH could be due to higher rates of weathering which cause natural acidification, thus increasing the rate at which Ga is released from mineral compounds into the exchangeable fraction. This may contribute to data from Watmough (2008) as natural soils in several different counties were used. In contrast, this study investigated variation from Ga and In freshly added to the soil, suggesting the effect of pH on retention could differ between natural environments, and contamination. Thus more studies involving spiking are required to properly assess the effect of pH on the relative mobility of Ga and In arising from extraction and e-waste.

5.1.1.3 Concentration added

The distribution coefficient unexpectedly increased with the concentration of Ga and In added to the extractant solution, though it plateaued within the upper half of the values tested. Total solution concentrations, thus mobility and bioavailability increased with addition to the extractant solution (Figure A. 4), though the relative increase in the immobilised fraction was larger. Generally, K_d decreases with increasing elemental concentrations, as sites capable of sorbing the investigated elements become saturated thus a larger fraction must remain in solution (Shaheen et al., 2013). Shaheen et al. (2015) measured 68.8-99.5% reductions in K_d when Zn application increased from 32.7 to 392.4 mg L^{-1} in solution across 11 soil types. Therefore, the increase in K_d observed on Figure 4.3 was unexpected and dissimilar to most trace elements.

Dominance of precipitation with relatively little adsorption is possibly explanatory for this trend. Above a threshold, precipitation and thus the concentration associated with the soil matrix increases, thus K_d increases as continually relatively less is present in the solution, though the total mobile concentration is little effected. For most trace elements, the distribution coefficient decreases with saturation of suitable sorption sites, but there is no quantitative evidence, within this study or literature, that adsorption plays a significant role in the behaviour of Ga and In. It was assumed to occur earlier (Chapter 2.1.2.2.1) utilizing evidence from other elements, but this study has demonstrated that even small differences in ionic radii and electronegativities caused drastic physical differences between Ga and In, thus assumptions are likely to not apply. The precipitation threshold

of both elements is extremely low (>0.03 µg L^{-1} α-GaOOH, pH 4.3 and 25°C modelled by Wood & Samson (2006); K_{sp} $10^{-73.24}$-10^{-15} measured $In(OH)_3$, In_2S_3, $In_2(CO_3)_3$ and $InPO_4$ reported by White & Hemond (2012)), increasing its importance in the system and the likelihood of this theory, though it cannot be verified. Staff et al. (2010) modelled that hydrolysis and species formed were not affected by concentration-speciation graphs for 4 mM and 0.07 mM Ga were identical-implying more total precipitation with concentration. Extractable Ga concentrations were just 0.5 mg L^{-1} different despite the industrial soil containing 49.1 mg kg^{-1} more, in research by Połedniok (2012), suggesting that excess above a threshold may have precipitated and contributed to the 175% larger oxide fraction. This theory could also be explanatory of the narrow concentration range in drainage and stream water within a Pb-Zn mine contaminated area, with 0.03-0.16 µg L^{-1} Ga and 0.02-0.04 µg L^{-1} In, despite soil In concentrations varying from 1.37-101 mg kg^{-1} (Ha et al., 2011). Indium water concentrations were equal to, with Ga slightly lower than the uncontaminated site (0.03 µg L^{-1} and 0.25 µg L^{-1} respectively).

Increased hydrolysis at high salt concentrations may also contribute to increased K_d, but insufficient measurements were completed to test this hypothesis. When hydrolysis occurs, hydrogen ions are released and the solution acidifies (Equation 2.1). The buffering capacity of the soil was assumed strong enough to prevent pH change, however pH was not measured within the concentration gradient. Acidification was associated with increased soil matrix association (Figure 4.2).

Variation in K_d observed by Watmough (2008) could be attributed to increasing concentration, in addition to the pH causation. Total concentrations of Ga increased with pH (R^2 = 0.28), thus could be partially responsible for increased K_d measurements with pH if the trend identified in this study applies across other environments. However, it is impossible to separate the effect of these two variables on the data supplied. Notably, the increase in matrix partitioning was particularly rapid from pH 4 to 5, close to the point of peak precipitation reported by Berstein (1998) and modelled on Figure 4.6, implying a dominating effect of precipitation within this range.

5.1.2 Comparison of data with previous literature

Despite limited measurement of Ga and In, this study and previous literature are in agreement these elements are strongly retained by the soil matrix. Less than 50% of both elements were present in the solution/exchangeable fraction in sequential extraction studies (Table 2.2 and Table 2.3). Distribution coefficient values varied dramatically, but data produced generally fell within the reported range, albeit on the low end of the scale. Across all treatments, In K_d ranged from 163-3187 with a mean of 860, almost fitting entirely within the 180-11,000 range across 112 Canadian soil types surveyed by Sheppard et al. (2007). Ga values were 82-689 (mean 310), of which three treatments (30 minute shaking time, 1 and 3 mg L^{-1}) fell below the minimum, with the measured

maximum less than all but one value in Table 2.4. However, due to variation in distribution coefficients across environments with a multitude of factors including pH, concentration, age and soil type, quantitative values are of lesser importance than a qualitative understanding of the direction in which they affect K_d, which the pH and concentration treatments in this study aimed to achieve. Knowledge has the potential application of aiding in reducing mobility, to ameliorate the risk of Ga and In leaving the contaminated soil.

5.1.3 Other factors affecting partitioning

5.1.3.1 Long time-scales

The degree of Ga and In soil matrix retention increases with time, and is believed the predominant reason why calculated K_d values were lower than most literature. Aging increases the crystallinity of Ga and In precipitates, and increases the capacity of trace element occlusion and absorption, with both processes decreasing solubility and causing K_d to rise (Wood & Samson, 2006). Figure A. 1 showed that retention increased with time, but the range was relatively short and didn't reach a peak. The length of time in even the highest treatment is much shorter than all data on Table 2.4 and Table 2.5. Hou et al. (2005) also spiked soil, but 18 months prior to measurement. Thus mobility of Ga and In contributed from contamination is expected to be greater than that in natural soils, which have indefinite time to form an equilibrium between the solid and solution phases, with leaching of many soluble compounds. Insufficient data is available to test this claim with Ga and In, but Sheppard et al. (2009) measured that K_d was 87.5% and 99.9% lower in soil spiked with Cl and I respectively before analysis, versus natural soil, though concentration was also likely a contributing factor.

5.1.3.2 Soil type/composition

Though not analysed in this study, differences in soil type have been extensively attributed to variation in K_d and mobility across literature, though difficult to compare due to the complexity of this parameter. Though pH was considered the overwhelming determinant factor, Sohlenius et al. (2013) showed that clay and Al were associated with increased retention of Ga (across various Swedish soils), and organic C with lesser retention, which was explanatory of the lower distribution coefficients in peat versus clayey soils. Theoretically, this was due to the close association between Ga and Al in clay minerals where the former is immobile, and similarities in the net charge (negative) between the dominating ionic species and sorption sites. If proved correct, this hypothesis will demonstrate that solid phase partitioning is significantly different between natural and anthropogenically added Ga and In; the latter is believed to be predominantly present in hydroxide precipitates and superficially adsorbed, as substitution into minerals is considered to be a slow process. Contrastingly, Sheppard et al. (2009) reported a much smaller distribution coefficient in a

clayey till than a peat soil (2600 versus 7800), but the former contained 25% DW (dry weight) $CaCO_3$ thus had a much higher pH, attributed in this study to decreased retention.

5.1.4 Presence of other elements

Though this study has investigated the mobility and behaviour of Ga and In, contamination is extremely unlikely to occur alone, thus other trace elements are expected to affect K_d and must be considered within the system. Abundance of geochemically associated and chalcophilic elements, such as Al, Zn, Fe, Cu, Pb and Sn, are also elevated when contamination arises from mining or extraction. 369-650% more soil In arising from Pb and Zn smelters was also associated with 300-1150%, 750-1180%, 1471-1765%, 61-90%, and 43-49% increments in Pb, Zn, Cd, Cu and Sn respectively, in a study conducted by Sterckeman et al. (2002). Gallium and In are predominantly utilized as alloys in electronic equipment and applications, particularly with the trace elements As and Sb (Ga) (Butcher & Brown, 2014), and As, Bi, Cd, Cu, Pb, Sb, Se, Sn and Te (In) (Schwarz-Schampera, 2014). A median of 140 mg kg^{-1} Ga in mobile phone printed circuit boards was accompanied by 330,000 mg kg^{-1} Cu, 19,000 mg kg^{-1} Ba, 13,000 mg kg^{-1} Pb, 2600 mg kg^{-1} Ta and 440 mg kg^{-1} Bi in data from Oguchi et al. (2011). Steinberger (1998) calculated that 16 µg kg^{-1} and 20 µg kg^{-1} increases in Ga and In soil concentrations from a damaged copper indium diselenide thin-film module were accompanied by 10 µg kg^{-1} Cu, 83 µg kg^{-1} Cd, 300 µg kg^{-1} Se, 2200 µg kg^{-1} Mo and 2200 µg kg^{-1} Zn.

5.1.4.1 Effect of other elements on partitioning

Sorption competition arising from labile forms of other trace elements is likely to reduce the distribution coefficients of Ga and In, though has not been analysed. Elements are prone to out-competition from suitable binding sites when similar or higher valency ions are present in solution, reducing the magnitude of retention to the soil matrix (Shaheen et al., 2013). Shaheen et al. (2013) measured 6.5-94.5% reductions in Cd K_d across a range of concentrations and soil types when elevated Zn was present, with the greater differences at high concentrations indicative that sorption competition was responsible (54-89% less at 224.8 mg L^{-1} solution Cd, versus -122 – 82% less at 28.1mg L^{-1} Cd). Theoretically mobility of Ga and In is also susceptible to increase from this factor. However, effects vary with pH and ionic charge-trivalent cations are accepted to bind more strongly than divalent-and is dependent on the contribution of sorption to distribution coefficient. Earlier discussion suggested that precipitation may contribute more than sorption, which is not unanimously expected to decrease via competition (predictions are complicated; precipitation may increase or decrease dependent on the species involved, with production of aqueous complexes (e.g. $InCl(OH)^{+}$), precipitated complexes (e.g. $InPO_4$), or out-competition and thus increased hydroxide precipitates).

No literature was found to appropriately compare the K_d of Ga or In between low and high concentrations of other elements.

5.1.4.1.1 Comparison of gallium and indium mobility to other elements

Though In was measured to be less mobile than Ga, there is insufficient data to feasibly compare mobility relative to other trace elements likely to enter the soil - plant system. Though K_d values have been calculated numerous times for most elements, this study demonstrated drastic variation with just three of many environmental factors-pH, concentration and time-emphasising the unsuitability of comparison across literature. None of the multi-elemental literature pieces uncovered compared K_d at the same concentration. Sheppard et al. (2009) and Watmough (2008) calculated distribution coefficients from natural soil background concentrations, but elemental ratios differ to mining residues and electronic equipment. Pb/In and Cu/In averaged 993 and 11 respectively in sites contaminated from a Pb-Zn mine, in contrast to 98 and 48 in uncontaminated sites (Ha et al., 2011). Sn/Ga and Sr/Ga values of 250 and 3 in mobile phone printed circuit boards (Oguchi et al., 2011) differ from 0.04 and 9, naturally in soil (Kabata-Pendias & Mukherjee, 2007). Sheppard et al. (2007) and Tyler & Olsson (2002) produced much higher K_d values for Ga than In (mean K_d Ga 11000 and 14211, with In 2800 and 967 respectively), opposite to the observations in this study. However, Ga and In retention was found to increase with concentration (Chapter 4.1.1.2). Both the soil matrix and solution in the latter study had less In than Ga (In: 0.029 mg kg^{-1} matrix 0.030 µg L^{-1} solution; Ga: 5.4 mg kg^{-1} matrix, 0.38 µg L^{-1} solution), in contrast to the identical concentrations in this experimentation. As Sheppard et al. (2007) used natural soil, Ga is also expected to be more abundant and possibly explanatory of the higher distribution coefficients.

5.2 Physiological uptake of gallium and indium by perennial ryegrass

Ryegrass was capable of taking up and translocating small but statistically significant ($p<0.001$) quantities of Ga and In into shoot biomass. Gallium reached a maximum of 11.57 mg kg^{-1} DM (dry matter), and In 0.015 mg kg^{-1} DM (Figure 4.7). Just three In treatments appeared to be above the detection limit (consistently increased above the control) (≥50 mg kg^{-1}), with all but one of the Ga treatments above that threshold (≥31.25 mg kg^{-1}). Uptake was consistently lower for In, even within the comparable concentration range (15.625-200 mg kg^{-1} soil addition). The mass of both elements in shoot biomass was extremely low compared to the mass applied (maximum of 0.013% Ga, 0.0021% In (Figure 4.8)), which is consistent with the findings from the previous section that both elements are highly immobile in soil, with In mobility lesser than Ga. However, two separate factors are involved; availability in soil, and capacity for shoot translocation. Due to the absence of a consensus on the oral toxicity threshold and food safety standard for each element, it cannot be evaluated whether these values are ‘high’ or ‘low’ in respect to the potential effect on the food chain.

Indium shoot concentrations plateaued within the range tested, but the exact cause is unknown. Uptake plateaued at 0.015 mg kg^{-1} DM, measured in soil spiked with 100 mg kg^{-1} In. Doubling concentrations produced an insignificantly small reduction (0.00019 mg kg^{-1}, $p>0.05$ in one-way ANOVA post-hoc LSD). The highest measurement in non-processed data was 0.021 mg kg^{-1}. Without further experimentation, it cannot be determined if this threshold is attributed to the maximum physiological capacity for In uptake, related to In availability in soil, or a result of toxicity (limiting the rate of further uptake). Data from Waterlot et al. (2013) shows that ryegrass was capable of containing higher concentrations of In. 0.0161-0.0509 mg kg^{-1} was recorded, despite much lower total soil concentrations than used in this study (0.23-0.54 mg kg^{-1}, versus 1.5625-200 mg kg^{-1}) and a similar experimental setup (6 week trials, sheltered from the environment). Thus bioaccumulation factors (BCF; concentration in plant/total concentration in soil) in this study were approximately two scales lower, and inferred much lower mobility in the soil-plant system. No other literature was found which measured In or Ga in ryegrass or pasture species.

Gallium uptake did not peak within this study. The highest concentration recorded was 13.65 mg kg^{-1}, with the slope indicative of increased uptake beyond the range measured. Thus, from the findings that total solution concentrations increased with addition (Figure A. 4), soil availability was a predominant factor limiting movement to foliage. Experimentation utilizing higher concentrations is required to identify when peak uptake occurs. Yu et al. (2015) and Syu et al. (2017) recorded maximum concentrations of ~48 mg kg^{-1} and 74 mg kg^{-1} respectively in rice seedlings exposed to 15-15.42 mg L^{-1}, also likely to continue beyond their ranges, however neither study is comparable due to physiological species differences and the hydroponic setup of both experiments. Syu et al. (2017) also measured peak In of 151 mg kg^{-1} in 10 mg L^{-1}. The recentness of these two studies, in addition to Chang et al. (2017) who investigated physiological responses to Ga toxicity, suggest that awareness of Ga and in contamination is increasing, with the potential for further findings in the upcoming years.

5.2.1 Effect of soil partitioning on plant uptake

Decreased soil mobility was calculated to be only partially responsible for lower concentrations of In than Ga, in ryegrass shoot biomass. As the soil used in this section of the study was the same type and unlimed, the pH and distribution coefficients were assumed to be the same as the T1 treatment in the batch sorption experiments; pH 5.54, K_d 689 Ga and 1266 In. As K_d was 46% smaller and thus a larger applied fraction remained in solution, it is unsurprising that Ga uptake was much higher than In. Sheppard et al. (2011) demonstrated that plant uptake was negatively correlated to K_d, with the R^2 of -0.45 particularly significant considering the variety in plant organs (roots, shoots and grains), species (wheat and barley) and essentially of elements included. However, when solution

concentrations were estimated from K_d (Figure 4.9), Ga uptake was still higher across most of the comparable concentration range (though poorly comparable due to the different trendline shapes). 2.23% Ga was estimated to be utilized versus 0.049% In at 0.039 mg in solution. Thus soil partitioning is not the only factor contributing to lesser In mobility in the system.

An estimate of the mass in solution could be calculated to aid in understanding, but is not accurate. Unfortunately, solution concentrations were not measured directly. The distribution coefficient varies with pH (Figure 4.2), and while assumed identical to T1 soil treatments no measurements were completed. K_d increases with concentration (Figure 4.3); 10 mg kg^{-1} in the extractant solution is equivalent to 60 mg kg^{-1} for the 5g of soil used, falling within the 1.5625-200 mg kg^{-1} In and 15.625-2000 mg kg^{-1} Ga ranges. Therefore, availability was underestimated at low concentrations, and overestimated at high. Retention increases with time (Figure A. 1), also contributing to overestimating availability. The total amount of biomass was not quantified; 1-2 cm height was left after harvesting and some material was lost in processing. Figure 4.9 contributes to our knowledge of Ga and In mobility in the system, but should only be used qualitatively.

Variation in soil mobility is likely a major contributor to the differences in plant:soil ratios in similar species within literature. This study and Waterlot et al. (2013) both measured In ryegrass shoot relative to total soil concentrations, but K_d was not calculated in the latter thus uptake relative to the bioavailable fraction could not be compared. Rapid retention of both elements, and variation across environments shows that total soil concentrations are poorly indicative of the concentration available for plant uptake. Indium's BCF was initially much smaller, but rose from a mean of 0.000586 to 1.50 when the estimated solution mass was considered, higher than their total soil BCF of 0.0814. Bioaccumulation factors were also scales higher (1738-4777% higher for Ga and In respectively) in data presented by Tyler (2005) regarding uptake by Beech forestry in a Haplic Podzol. High soil mobility is believed responsible; though not measured, K_d is expected to be relatively low. pH was 3.2-3.6, where Figure 4.5 and Figure 4.6 predict just 0.01-0.17% of precipitation-prone $In(OH)_3$ to be present, and 69-84% of maximum Ga precipitation. Soil was an O horizon, abundant in organic carbon, which Sohlenius et al. (2013) associated with decreased retention. Ha et al. (2011) demonstrated that physiological differences between species was also a contributing factor, but In BCFs were the same scale for the four plant types tested (approximately 0.14-0.20).

5.2.2 Causes of low plant uptake

Despite no evidence that ryegrass uptake was close to peaking, the fraction of bioavailable Ga present in shoot biomass was extremely low-a maximum of 9.19%. Even accounting for experimental error and inaccuracy in the K_d value used, this value is particularly small. Thus it is implied that other

physical processes or plant physiology restricts movement into the shoot. Though insufficient data was produced for verification, three likely causes are outlined below.

5.2.2.1 Leaching of gallium and indium from soil

Gallium and In have a small capacity to be leached from soil, though not investigated nor believed largely responsible for low plant uptake. In solution, elements have the capacity to move downwards through the soil profile, and may be removed via groundwater. Anions are generally more susceptible, due to the predominantly net negative charge. This pathway of removal was not evaluated in this study. The likelihood of leaching is expected to be low relative to other elements, due to the strong association of Ga and In with the soil matrix. Two studies have demonstrated the capacity of this process. Hou et al. (2005) measured that ≤40% of artificially applied soluble In leached from a 35 cm soil column in 18 months, and only 5-38% had moved below the top 2 cm. Total Ga was reportedly 7.24 mg kg^{-1} higher in the upper B versus the overlying E horizon in a Haplic Podzol analysed by Tyler (2004b), with long time periods and extensive weathering responsible for this movement. Leaching is not believed to be significant in this study; saucers collected leachate (retaining aqueous species in the system), and the root network was extensive and believed to penetrate most of the soil, as evidenced by extrusions from the bottom of the pots for most treatments.

5.2.2.2 Increased retention of gallium and indium to the soil matrix

Mobility and thus bioavailability were shown to reduce with time (Figure A. 1). There was a huge temporal difference between the 120 minute time period used to calculate the distribution coefficient, and the 7 week duration in this section of the study, inclusive of 7 days before seeds were planted. Cumulative increases in retention are believed to have occurred, but the magnitude is unknown.

5.2.2.3 Retention of gallium and indium in root biomass

The predominant cause of low movement to shoots is believed to be root retention. Strong sorption to outer root cells is the best understood physiological process, severely limiting movement into above-ground biomass (Chapter 2.2.1). Thus in the little suitable literature, shoot:root concentration ratios are usually below 1 (Table 2.8 and Table 2.9). Data is of similar scale to the shoot:soil solution ratios in this study (<0.01-1.71 shoot:root, versus shoot:soil solution of 0.017-0.092 Ga, 0.00049-0.026 In), implying that most unaccounted matter could be retained in roots, despite an absence of root concentration measurements. Syu et al. (2017) and Yu et al. (2015) are recent examples which clearly demonstrate extensive root retention in rice seedlings; the former reported a tenfold increase in root relative to shoot Ga and In, with the latter reporting that 98.2% of plant Ga was found in the roots.

5.2.3 Relationship between uptake of gallium, indium and other elements

5.2.3.1 Nutrient deficiencies observed

Nitrogen deficiencies were experiences in treatments containing In and low concentrations of Ga. Nitrate was the anion in the salts used, with 3 units per unit of Ga or In applied. Nitrogen levels in the soil were insufficient for optimum plant growth as the experiment progressed, thus after 3 weeks pots with high concentrations of NO_3^- added, partially 500, 1000 and 2000 mg kg^{-1} Ga, had visibly higher growth rates and greener leaves (indicative of more chlorophyll and higher photosynthetic rates). Deficiencies were not ameliorated via urea until 4 weeks after sowing, and as they were of the severity to produce visual symptoms, large physiological disruptions had occurred. Foliar analysis was not completed, but the reversal of symptoms when urea was applied and absence of symptoms from treatments with ≥1000 mg kg^{-1} $Ga(NO_3)_3$ are clear evidence that N was limiting. Thus the severity of N deficiency varied across treatments, in addition to exposure to Ga and In.

Phosphorus deficiency is also believed to have occurred, but the initial supply was consistent across treatments. Relatively late in the experiment purpling was observed at the base of shoots of most treatments, with several purple leaves observed in treatments with large biomasses, a common deficiency symptom (McLaren & Cameron, 1996). Supply (forms and concentrations initially present in the soil) was the same across all treatments. Inconsistencies were observed and symptoms more pronounced in the highest Ga treatments, due to the relatively higher biomass arising from the absence of N deficiency.

Water stress was inconsistent across treatments, also attributed to nitrogen availability. Transpirational potential and water requirements increase with leaf area, usually closely correlated to total biomass. As the experiment progressed, the treatments with the highest biomass-high Ga- had consistently lesser, then an absence of water in saucers when checked daily. The predominant physiological effect is reduced biomass accumulation (decreased leaf area to intercept light, and decreased CO_2 entry through stomatal closure), though osmotic adjustment also occurs in many species and alters the partitioning of elements and compounds within the plant.

5.2.3.1.1 Effect of nutrient deficiencies on elemental correlation data

Details of the variation in elemental concentrations between treatments cannot be used to understand the effect of Ga and In, due to the nitrogen deficiencies experienced. Several strong correlations were observed (Table 4.3 and Table 4.4) with Mg and Ca uptake particularly closely related to Ga (R^2 0.797 and 0.641 respectively), as determined by the concentration of $Ga(NO_3)_3$ added to soil. The effect of the second independent variable, N availability, on elemental uptake could not be separated from the variation attributed to Ga and In. Interactions between elements (increased or reduced uptake of macronutrients, micronutrients or toxic contaminants) could be

important to plant growth rates and the heath of animals consuming the product. Table 5.1 compares differences in nutrient uptake between this study and Syu et al. (2017). As the latter reportedly had consistent and sufficient nutrients, the differences in trends could be attributed to higher nitrogen uptake; particularly reductions in shoot K, and increased Mg, Ca and Zn, though cannot be verified.

Table 5.1 Differences in rice and ryegrass shoot nutrient concentrations, under high and low Ga and In treatments. Highest and lowest Ga and In treatments were 0-15 mg L^{-1} Ga and 0-10 mg L^{-1} In Syu et al. (2017); 0-2000 mg kg^{-1} Ga and 0-200 mg kg^{-1} In this study. Shaded cells were significantly different (p<0.05) in one-way ANOVA LSD tests.

Element		K	Mg	Ca	Fe	Zn	Mn
Difference from lowest (%)	Gallium; Syu et al. (2017)	11.2	1.6	3.4	-57.0	-12.9	22.7
	Gallium; this study	-42.8	101.1	91.1	-58.6	120.3	94.6
	Indium; Syu et al. (2017)	-5.5	-35.9	-38.9	-48.8	-19.5	-11.7
	Indium; this study	2.3	31.4	36.0	-27.9	60.6	-4.0

5.2.3.2 Effect of gallium on iron uptake

Addition of Ga significantly reduced the concentration of Fe in ryegrass shoots. Uptake decreased exponentially, with reductions peaking at 59-64% when Ga concentrations rose above 3 mg kg^{-1} (Figure 4.10). Due to findings in previous literature (Chapter 2.2.4), this relationship is believed predominantly attributed to Ga, versus NO_3^-. The absence of a consistent strong trend with In (Figure 4.11) further increases the likelihood that replacement in phytosiderophores and other Fe^{3+} physiological compounds is responsible. Syu et al. (2017) also measured large Fe shoot reductions, in Strategy II rice plants placed in a Ga solution. Their trend was less consistent-57% less was observed in 1 and 15 mg L^{-1} Ga, with just 41% in 5 and 10 mg L^{-1}-but significant, and may have plateaued at <1 mg L^{-1}. Unlike this study, reductions were also observed under elevated In, but this was probably related to rhizotoxicity, restricting the rooting area and total nutrient availability.

Both sets of experiments had few repeats, which limited data accuracy and trendline fit, but was sufficient for interpretation of trends to achieve the aims. Just 3 samples were completed for each batch sorption treatment, and 4 for each plant uptake treatment. Thus possible outliers could not justifiably be removed, as there was not enough evidence to establish an accurate threshold between natural variation, natural anomalies, and methodological error. Each measurement had large leverage, thus possible outliers significantly reduced the accuracy of the data produced. Mean Ga K_d at pH 5.54 increased from 689 to 809 when one measurement (448) was removed, and the concentration of In in control shoot biomass decreased from 0.0058 mg kg^{-1} to 0.0025 mg kg^{-1} with removal of a 0.016 mg kg^{-1} measurement. Though this likely contributed to low R^2 values for many trendlines (such as In in Figure 4.3), figures were able to effectively qualitatively evaluate the capacity for soil retention and plant uptake, and show the response to the treatments. Accuracy of

quantitative values was of relatively little importance, particularly for K_d, as Chapter 5.1.2.2.2 demonstrated that it couldn't be feasibly compared across various environments. Nitrogen deficiencies more severely reduced the quality of data produced in plant experimentation.

5.2.4 Phytotoxicity

Potential toxicity symptoms were not able to be identified and isolated in this study, due to the variation in growth and physiology attributed to nitrogen deficiencies. Excessive Ga and In availability is accepted to cause reductions in root and shoot biomass through strong sorption to outer root cells, reducing water and nutrient uptake (Chapter 2.2.2). In this study, biomass variation was not able to be delineated between the effects attributed to elevated Ga and In, versus those related to nitrogen availability, thus was not analysed. Toxicity-induced growth rate reductions greatly reduce mobility in the plant aspect of the system, movement of these elements into the food chain, and the capacity for contaminated land to be used for agriculture; therefore it is an important area to research. Syu et al. (2017) attributed a plateau in the total mass of In in rice seedlings to toxicity, with reductions in root biomass theoretically limiting uptake of In and other essential elements. Thus toxicity may be responsible for In uptake plateauing at 0.015 mg kg^{-1} in this study, particularly since Waterlot et al. (2013) showed that ryegrass is capable of containing up to 0.0509 mg kg^{-1} In, but cannot be verified from the nitrate effect.

Previous studies suggest that In has a lower toxicity threshold than Ga, which may further contribute to higher uptake of Ga. Lesser rhizotoxicity theoretically allows greater total uptake (via optimal physiological root functioning and larger area of soil covered) and translocation to shoot biomass. Research comparing these two elements in identical environments is limited, but all applicable papers agreed with this claim. Syu et al. (2017) found that 0.08 mg L^{-1} In in solution caused statistically significant reductions in root and shoot length and biomass, with 15 mg L^{-1} Ga increasing the size of all four components. Kopittke et al. (2009) recorded reductions in root elongation at 0.36 μM In versus 0.67 μM Ga, with 50% reductions in elongation rate at 0.72 μM and 0.90 μM respectively. Clarkson (1965) observed greater reductions in root elongation rates from Ga, but 50% high concentrations were added with just 22% lesser elongation. Hydrolysis is hypothesised to be a partial underlying cause; In^{3+} is abundant in a much larger pH range than Ga^{3+} (the predominant rhizotoxic speciation; Chapter 2.2.2), with >10% in this form at pH ≤4.7 versus Ga with a ≤4.1 10% threshold, as modelled by Minteq (Figure 4.4 and Figure 4.5). Minteq also predicted trivalent In to be 10-fold that of Ga within the pH range of 4.8-5.0 employed by Syu et al. (2017) (though not adjusted for other species present in that study). Table 2.10 and Table 2.11 shows that there is not enough toxicity data, for either element, to form a threshold consensus.

5.2.5 Comparison with other contaminants

Contamination is extremely unlikely to only involve Ga and In, thus physiological interactions with other contaminants are expected in the environment. Chapter 5.1.2.2 listed several key elements also likely to enter the system via processing or product disposal, though many more are susceptible, dependant on the composition of mineral deposits and waste products. In addition to the direct effects of associated elements on shoot biomass composition and growth rates, uptake of Ga and In may be affected, along with the potential for biomass concentrations to cross their toxicity thresholds. Arsenic, the element used in the most common Ga alloy, reduced the root length of lentil from ~3000cm to ~1000cm when 10 mg L^{-1} was present in irrigation water (Ahmed, 2006), which would likely decrease total availability and thus shoot concentrations of Ga if also added in the system. Organic acids are frequently produced in response to Al toxicity, believed capable of also binding and restricting uptake of Ga and In (Chapter 2.2.3). Many other examples are present. However, no papers were found to directly investigate Ga and In uptake relative to spiking of other elements. This study and other recent research have investigated Ga and in mobility and physiological interactions, but the next step is to evaluate their potential risk relative to other contaminants.

5.3 Other pathways of transport of gallium and indium to the food chain

As movement from soil to shoot biomass was found to be very little, physiological uptake is unlikely to be a major source of Ga and In to the food chain, but there is the possibility for oral ingestion via other pathways.

5.3.1 Atmospheric deposition on foliage

Large quantities of Ga and In may be deposited on foliage as aerosols, and is a likely pathway, particularly near industrial sites or urban areas. Both elements are naturally present at low concentrations in the atmosphere (<0.001 ng m^{-3} Ga and <0.08 ng m^{-3} In) but are anthropogenically elevated through mining, smelting, product manufacture and coal burning, with up to 1 ng m^{-3} Ga and 1200 ng m^{-3} In reported (Kabata-Pendias & Mukherjee, 2007; White & Hemond, 2012). Thus atmospheric deposition is likely to be a major source, if Ga and In are retained during transport (not easily removed by rainwater or in food processing). There is an absence of literature suitably demonstrating this, particularly its importance in comparison to physiological uptake, but is theoretically possible. A lack of measurements of natural plant uptake (Table 2.6 and Table 2.7) limits the ability to determine if elevated concentrations near processing plants are due to atmospheric deposition. Tyler (2005) found that in beech leaves, ≥21% of Ga was deposited as it was able to be removed by washing. In a Norway moss survey, 76% of the variation in Ga concentration was explained by its proximity to an Al smelter (Berg & Steinnes, 1997). Mean Ga and In Swedish moss

concentrations varied 0.30-0.09 mg kg^{-1} and 0.0110-0.0013 mg kg^{-1} in 1975-2000, attributed to the degree of aerosol production (Rühling & Tyler, 2004).

5.3.2 Presence in drinking water

Regardless of their capacity for entry, due to their poor solubility drinking water is unlikely to be a major source of Ga and In. Both elements are naturally present at low concentrations in waterbodies (e.g. 11-15 pmol kg^{-1} dissolved Ga and 0.07-4.5 pmol kg^{-1} In in oceanic basins (Alibo et al., 1999)), but are capable of increased entry through soil leaching (Chapter 5.2.2.1) or atmospheric deposition (White & Hemond, 2012). However, due to their poor solubility, upon entry Ga and In are predicted to readily precipitate. Particularly low concentrations are expected in drinking water. The aesthetically recommended pH range is 7.0-8.5 (Ministry of Health, 2008), which falls within the peak precipitation range of In (~4.5-9, Wood & Samson (2006)) with relatively reasonably high precipitation of Ga (Figure 4.6; 1 µM solubility calculated by Bernstein (1998)), with precipitates likely removed via filtration. Further research is required to verify this claim. The concentration of Ga dissolved, relative to the concentration associated with suspended solids was extremely low in Californian streams sampled by Shiller & Frilot (1996), at 4.72×10^{-8} - 2.59×10^{-7}.

Chapter 6

Conclusions

This study aimed to determine the mobility of Ga and In in the soil-plant system, through investigation of their strength of retention to the soil matrix and capacity for uptake by perennial ryegrass. Both elements were found be poorly mobile, with relatively little present in the soil solution, and low rates of transport from soil to shoot biomass.

Immobilisation to the soil matrix is rapid, increases with acidity, and proportionally increases with the concentration of soluble Ga and In applied. Average distribution coefficients were approximately 400 and 2000 for Ga and In respectively. Precipitation of poorly-soluble, neutral hydroxide compounds produced by hydrolysis is believed to be a major contributing factor, particularly causing K_d to increase with concentration. Formation of the poorly-sorbed anionic species is likely responsible for K_d decreasing with pH.

Translocation to shoot biomass is extremely low, relative to the abundance in soil and the soil solution. The mass in harvested foliage proportional to application peaked at 0.013% Ga and 0.0021% In. Strong retention within roots is believed to greatly reduce mobility. Additionally, bioavailable Ga significantly reduces Fe uptake.

Gallium has a greater mobility than In in the soil-plant system. Lesser matrix partitioning (averge K_d 1600 smaller) and higher translocation (0.48 mg kg^{-1} at 125 mg kg^{-1} added to soil, versus 0.015 mg kg^{-1} In at 100-200 mg kg^{-1}) were calculated in identical environments.

Overall, there is little risk of Ga and In contaminants entering the food chain via physiological plant uptake, with both elements predicted to accumulate in the upper soil profile.

Future research should verify that the trends identified, both regarding soil mobility and plant uptake, are replicable across many environmental conditions (with variation in pH, concentration, time, clay and organic carbon content), and extent beyond the ranges tested in this study. Data collection involving phytotoxicity, root and shoot concentrations across a range of plant species is recommended, to fully evaluate the capacity for Ga and In to enter the food chain under severe contamination. Retention and uptake dynamics should be investigated under elevated concentrations of associated elements-such as As, Zn, Fe, Cu, Pb and Sn-to assess the relative toxicity of Ga and In, and predict the effects of contamination with higher accuracy.

Appendix A

A.1 Materials and methods

A.1.1 Calculation of K_d

$$M = C_a \times (V_a/1000)$$

Equation A. 1 Calculation of extractant mass. M = mass of extractant in extract (µg), C_a = extractant concentration with acid (µg L^{-1}), V_a = volume of extract and acid (mL).

$$C = (M/(V/1000)) \times 5$$

Equation A. 2 Calculation of the extractant concentration. C = extractant concentration (µg L^{-1}), V = volume of extract (mL).

Solution correction factors, found from Figure A. 2 and Figure A. 3.

$$C_c = 4.3493 \times C^{0.7015}$$

Equation A. 3 Ga correction factor. C_c = corrected concentration (mg L^{-1}), C = extractant concentration (mg L^{-1}).

$$C_c = 4.4355 \times C^{0.6785}$$

Equation A. 4 In correction factor. C_c = corrected concentration (mg L^{-1}), C = extractant concentration (mg L^{-1}).

$$S = ((C_i - C_c) \times (V/1000))/0.005$$

Equation A. 5 Calculation of the soil matrix-bound concentration. S = soil matrix concentration (mg kg^{-1}), C_i = concentration in $Ca(NO_3)_2$ solution.

$$K_d = S/C_c$$

Equation A. 6 Calculation of K_d.

A.1.2 Calculation of ryegrass shoot elemental concentrations

Elements measured: Ga, In, B, Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Zr, Nb, Mo, Cd, Sb, Ta, W, Re, Pb, Rh.

$$C_p = ((C_m - C_b) \times 5 \times V_d)/M_s$$

Equation A. 7 Calculation of ryegrass shoot elemental concentrations. C_p = shoot concentration (µg kg^{-1}), C_m = ICPMS concentration (µg L^{-1}), C_b = average of ICPMS blanks (µg L^{-1}), V_d = digest volume (mL), M_s = sample mass (g).

A.1.3 Effect of shaking time and K_d

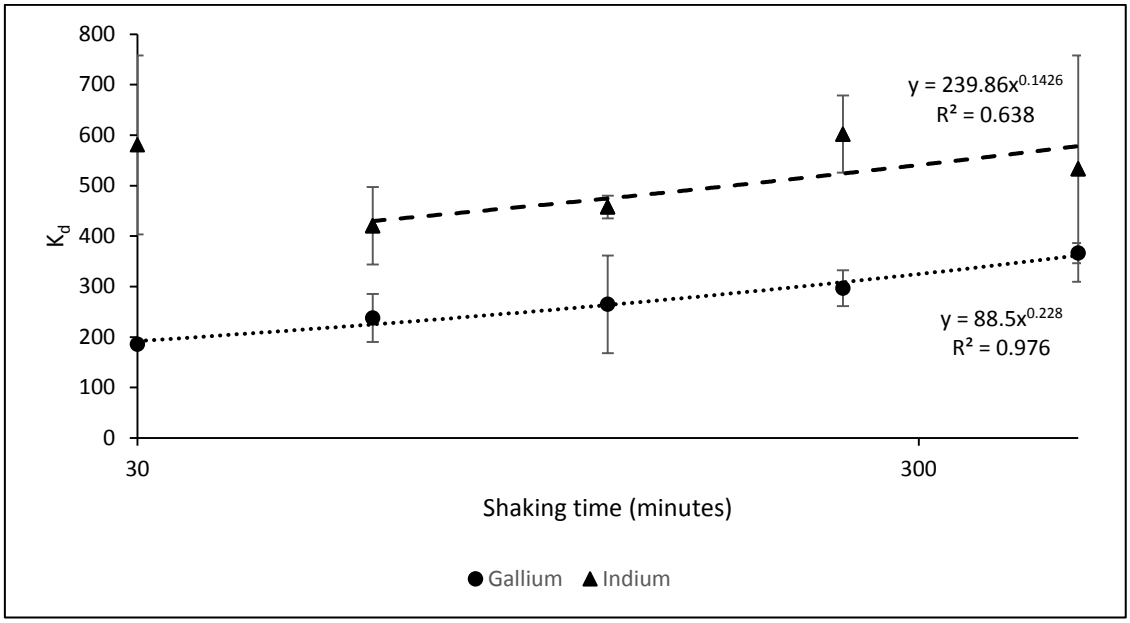

Figure A. 1 Effect of shaking time on K_d. Mean values of each treatment presented. Error bars denote standard deviation of K_d for each shaking time category (*n*=3). In trendline does not include 30 minute treatment.

A.1.4 Measurement of soil solution pH

Table A. 1 Lime application and pH of extractant solutions for each soil treatment. Lime application data from Valentinuzzi et al. (2015). pH measured with a pH electrode in 5 g soil shaken with 30 mL un-spiked $Ca(NO_3)_2$ extractant solution for 120 minutes.

Soil treatment	Lime applied (wt%)	pH			
		Sample 1	Sample 2	Sample 3	Average
T1	0	5.53	5.54	5.54	5.54
T2	0.31	6.05	6.03	6.03	6.04
T3	0.61	6.79	6.81	6.81	6.80
T4	1.25	7.01	7.03	7.03	7.02
T7	10.00	7.11	7.14	7.16	7.14
No soil	-	5.31	5.29	5.4	5.33

A.1.5 Identification of correction factors

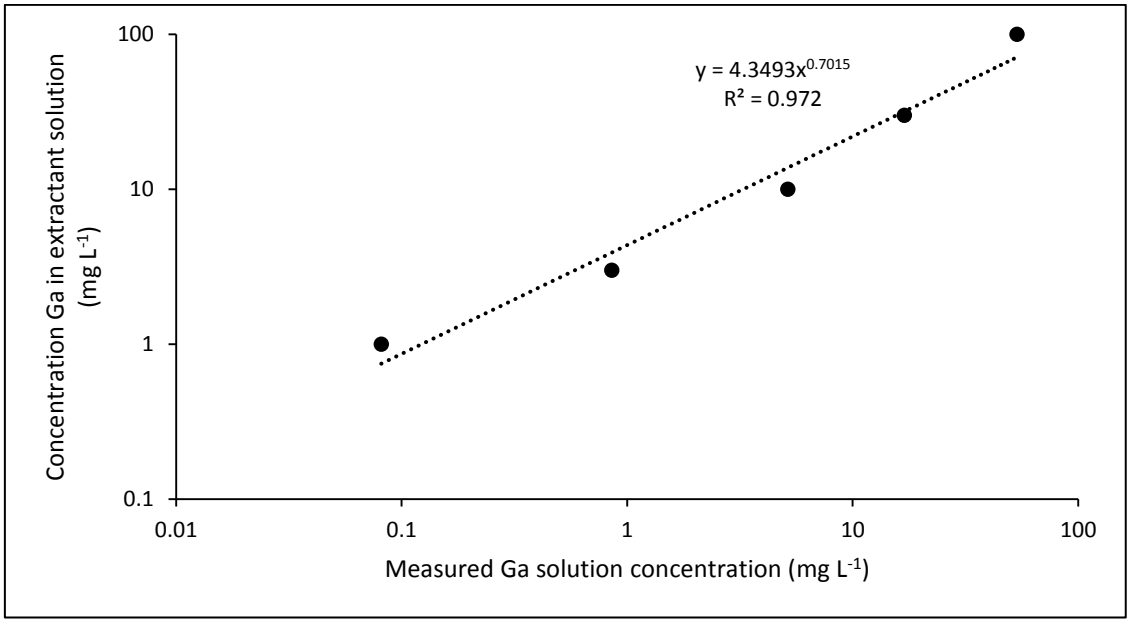

Figure A. 2 Identification of the Ga correction factor. Mean solution concentrations of concentration gradient treatments without soil plotted on the x-axis (*n*=3).

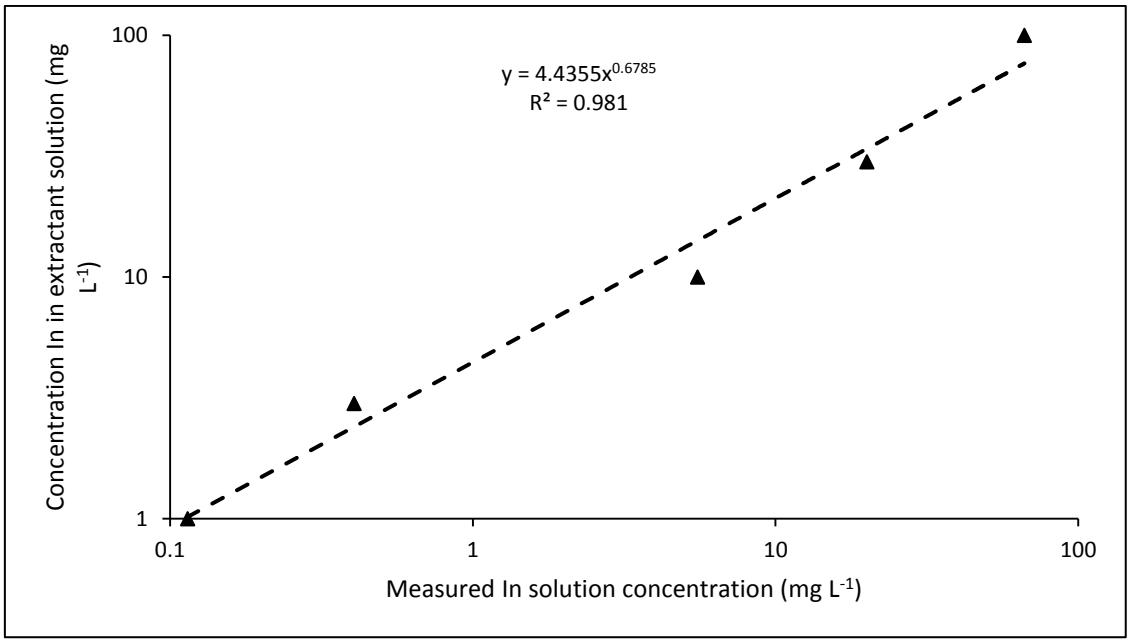

Figure A. 3 Identification of the In correction factor. Mean solution concentrations of concentration gradient treatments without soil plotted on the x-axis (*n*=3).

A.1.6 Parameters used in the MINTEQ model

Table A. 2 Species inputted and parameters on the Visual MINTEQ 3.1 models.

Species	Concentration
Ca^{2+}	0.05 M
NO_3^-	0.100484 M
Ga^{3+}/In^{3+}	10 mg L^{-1}
CO_2	0.00038 atm
Temperature	20°C
pH measurement interval	0.1

A.2 Results

A.2.1 Distribution coefficient data

Table A. 3 Mean distribution coefficients of Ga and In for each treatment.

Treatment	Mean K_d gallium	Mean K_d indium
Shaking time gradient		
30min	186	581
60min	238	421
120min	265	458
240min	297	602
480min	366	534
pH gradient		
T1, 5.54	689	1266
T2, 6.04	485	983
T3, 6.80	360	910
T4, 7.02	344	679
T7, 7.14	265	458
Concentration gradient		
1 mg L^{-1}	88	163
3 mg L^{-1}	82	339
10 mg L^{-1}	265	458
30 mg L^{-1}	280	1812
100 mg L^{-1}	392	3187

A.2.2 Variation in solution concentrations with added gallium and indium

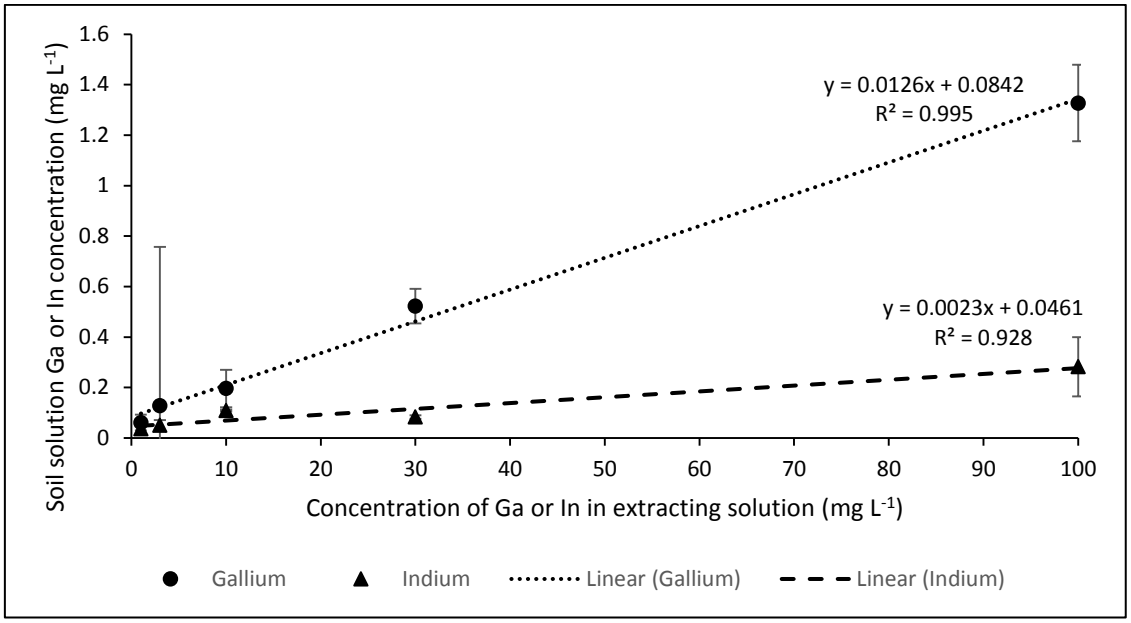

Figure A. 4 Effect of the concentration of Ga and In added to the $Ca(NO_3)_2$ extracting solution on the concentration in the soil solution. Mean values of each treatment presented (*n*=3). Error bars denote standard deviation of soil solution concentrations for each category. Plant uptake data, normal axes

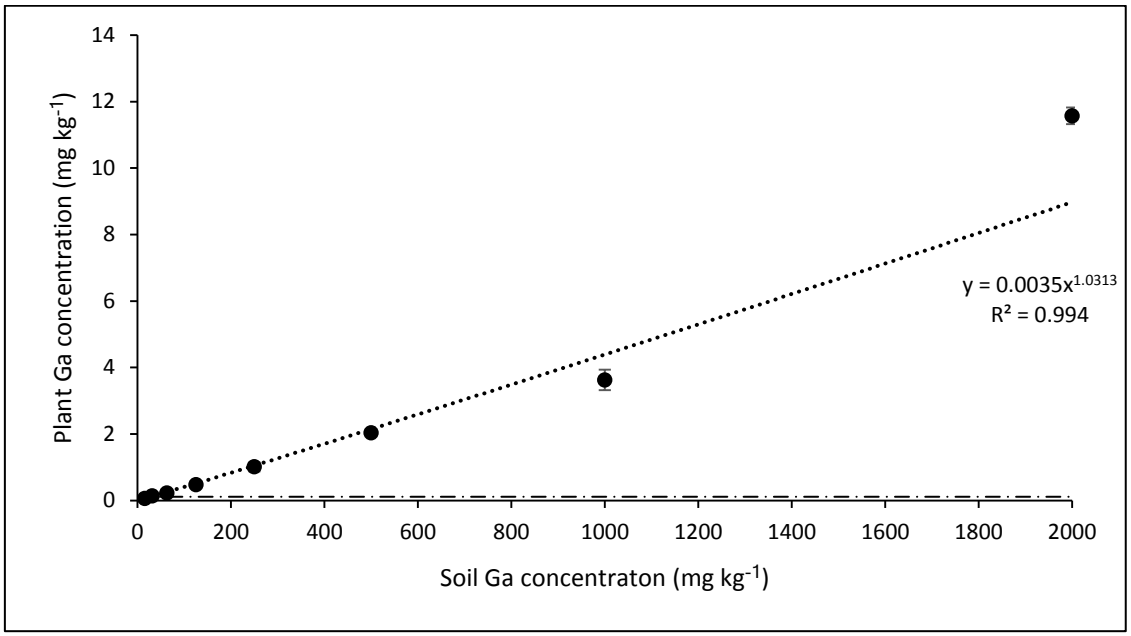

Figure A. 5 Effect of the concentration of Ga added to soil on ryegrass shoot concentrations, non-logarithmic axis. Mean values of each treatment presented (*n*=4). Error bars denote standard deviation of biomass concentration for each category. Detection limit assumed equal to control (dashed line), 0.11 mg kg^{-1} DM Ga. Control value not included in the trendline.

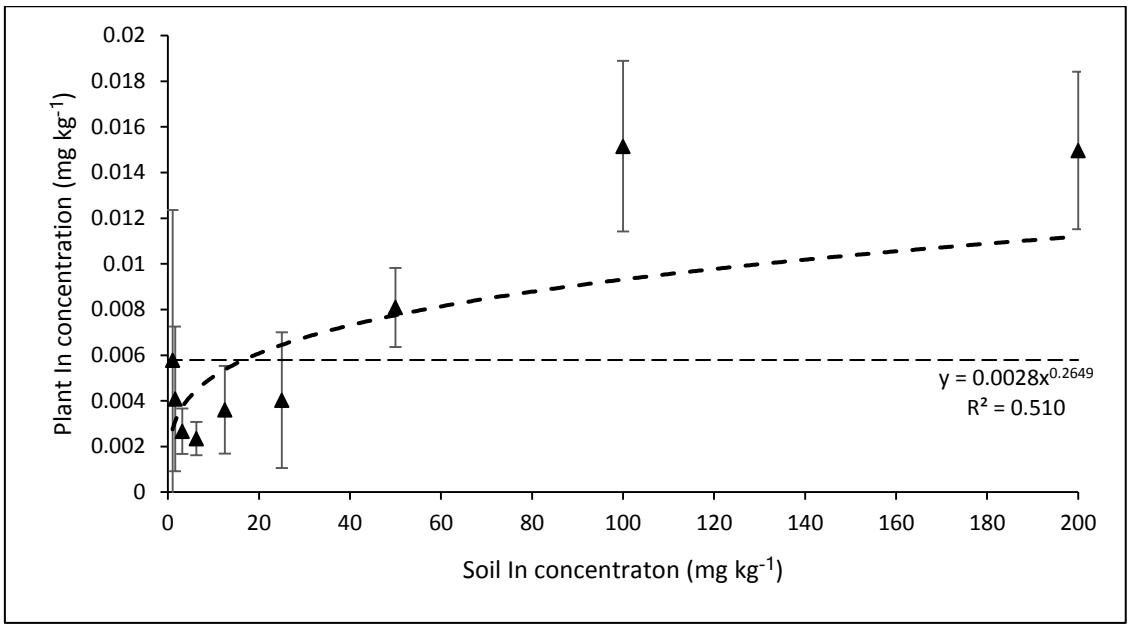

Figure A. 6 Effect of the concentration of In added to soil on ryegrass shoot concentrations, non-logarithmic axis. Mean values of each treatment presented (*n*=4). Error bars denote standard deviation of biomass concentration for each category. Detection limit assumed equal to control (dashed line), 0.0.0058 mg kg^{-1} DM In. Control value not included in the trendline.

References

Ahmed, F., Killham, K., & Alexander, I. (2006). Influences of arbuscular mycorrhizal fungus *Glomus mosseae* on growth and nutrition of lentil irrigated with arsenic contaminated water. *Plant and Soil, 283*(1) 33-41. doi:10.1007/s11104-005-0415-8

Al Mamun, S., Chanson, G., Muliadi., Benyas, E., Aktar, M., Lehto, N., … Robinson, B. (2016). Municipal composts reduce the transfer of Cd from soil to vegetables. *Environmental Pollution, 213*, 8-15. https://doi.org/10.1016/j.envpol.2016.01.072

Alibo, D. S., Nozaki, Y., & Jeandel, C. (1999). Indium and yttrium in North Atlantic and Mediterranean waters: comparison to the Pacific data. *Geochimica et Cosmochimica Acta, 63*(13-14), 1991–1999. https://doi-org.ezproxy.lincoln.ac.nz/10.1016/S0016-7037(99)00080-0

Alloway, B. J. (2013). *Heavy metals in soils, Trace metals and metalloids in soils and their bioavailability* (3rd ed). Retrieved from http://link.springer.com/book/10.1007/978-94-007-4470-7

Audi, G., Bersillon, O., Blachot, J., & Wapstra, A. H. (2003). The Nubase evaluation of nuclear and decay properties. *Nuclear Physics A, 729*(1), 3-128. https://doi.org/10.1016/j.nuclphysa.2003.11.001

Babula, P., Adam, V., Opatrilova., R., Zehnalek, J., Havel, L., & Kizek, R. (2008). Uncommon heavy metals, metalloids and their plant toxicity: a review. *Environmental Chemistry Letters, 6*(4), 189-213. doi:10.1007/s10311-008-0159-9

Banin, A., Navrot, J., Noi, Y., Yoles, D. (1981). Accumulation of heavy metals in arid-zone soils irrigated with treated sewage effluents and their uptake by Rhodes grass. *Journal of Environmental Quality, 10*(4), 536-540. doi:10.2134/jeq1981.00472425001000040024x

Barbalace, K. (2007). *Periodic table of elements - Sorted by atomic mass average.* Retrieved from https://environmentalchemistry.com/yogi/periodic/mass.html

Barbalace, K. (2007). *Periodic table of elements - Sorted by electronegativity (Pauling).* Retrieved from https://environmentalchemistry.com/yogi/periodic/electronegativity.html

Barysz, M., Leszczynski, J., & Bilewicz, A. (2004). Hydrolysis of the heavy metal cations: Relativistic effects. *Physical Chemistry Chemical Physics, 6*(19), 4553-4557. doi: 10.1039/B408406C

Bénézeth, P., Diakonov, I. I., Pokrovski, G. S., Dandurand, J., Schott, J., & Khodakovsky, I. L. (1997). Gallium speciation in aqueous solution. Experimental study and modelling: Part 2. Solubility of α-GaOOH in acidic solutions from 150 to 250°C and hydrolysis constants of gallium (III) to 300°C. *Geochimica et Cosmochimica Acta, 61*(7), 1345-1357. https://doi.org/10.1016/S0016-7037(97)00012-4

Berg, T., & Steinnes, E. (1997). Recent trends in atmospheric deposition of trace elements in Norway as evident from the 1995 moss survey. *Science of The Total Environment, 208*(3), 197-206. https://doi.org/10.1016/S0048-9697(97)00253-2

Bernstein, L. R. (1998). Mechanisms of Therapeutic Activity for Gallium. *Pharmacological Reviews, 50*(4), 665-682. Retrieved from http://pharmrev.aspetjournals.org/content/50/4/665

Bernstein, L. R. (2005). 31Ga Therapeutic gallium compounds. In M. Gielen & E. R. T. Tiekink (Eds.), *Metallotherapeutic drugs and metal-based diagnostic agents: The use of metals in medicine.* Retrieved from https://www.gallixa.com/GAMReferences/MetallotherapeuticsChapter14.pdf

Bhavan, I. (2016). Gallium. *Indian Minerals Yearbook 2014 (Part- II : Metals & Alloys).* Retrieved from http://ibm.nic.in/writereaddata/files/05312016123600Final_IMYB-Gallium-2014.pdf

Biology For Life. (n.d.). *Correlations.* Retrieved from https://www.biologyforlife.com/correlation.html

Boros, E., Marquez, B. V., Ikotun, O. F., Lapi, S. E., & Ferreira, C. L. (2014). Coordination chemistry and ligand design in the development of metal based radiopharmaceuticals. In T. Storr (Ed.), *Ligand design in medicinal inorganic chemistry.* Retrieved from https://ebookcentral.proquest.com/lib/lincoln-ebooks/reader.action?docID=1683802#

Boughriet, A., Proix, N., Billon, G., Recourt, P., & Ouddane, B. (2007). Environmental impacts of heavy metal discharges from a smelter in Deûle-canal sediments (northern France): Concentration levels and chemical fractionation. *Water, Air, and Soil Pollution, 180*(1-4), 83–95. doi:10.1007/s11270-006-9252-5

Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science, 277*(1), 1-18. doi:10.1016/j.jcis.2004.04.005

Brautigan, D., Rengasamy, P., & Chittleborough, D. (2012). Aluminium speciation and phytotoxicity in alkaline soils. *Plant and Soil, 360*(1), 187-196. doi:10.1007/s11104-012-1232-5

Brunner, I., & Sperisen, C. (2013). Aluminum exclusion and aluminum tolerance in woody plants. *Frontiers in Plant Science, 4,* 1-12. doi:10.3389/fpls.2013.00172

Butcher, T., & Brown, T. (2014). Gallium. In G. Gunn (Eds), *Critical metals handbook* (pp. 150-176). Retrieved from https://ebookcentral.proquest.com/lib/lincoln-ebooks/reader.action?docID=1594545

Chang, H., Wang, S., & Yeh, K. (2017). Effect of gallium exposure in Arabidopsis thaliana is similar to aluminum stress. *Environmental Science and Technology, 51*(3), 1241-1248. doi:10.1021/acs.est.6b05760

Clarkson, D. T. (1965). The Effect of Aluminium and some other Trivalent Metal Cations on Cell Division in the Root Apices of Allium cepa. *Annals of Botany, 29*(2), 309–315. https://doi.org/10.1093/oxfordjournals.aob.a083953

Cobelo-García, A., Filella, M., Croot, P., Frazzoli, C., Laing, G., Ospina-Alvarez, N., … Zimmermann, S. (2015). COST action TD1407: network on technology-critical elements (NOTICE)—from environmental processes to human health threats. *Environmental Science and Pollution Research, 22*(19), 15188–15194. doi:10.1007/s11356-015-5221-0

DeSutter, T. M., & Godsey, C. B. (2010). Sugar-beet-processing lime as an amendment for low pH soils. *Communications in Soil Science and Plant Analysis, 41*(15), 1789-1796. doi:10.1080/00103624.2010.492065

Diakonov, I. I., Pokrovski, G. S., Bénézeth, P., Schott, J., Dandurand, J., & Escalier, J. (1997). Gallium speciation in aqueous solution. Experimental study and modelling: Part 1. Thermodynamic properties of Ga(OH)4− to 300°C. *Geochimica et Cosmochimica Acta, 61*(7), 1333-1343. https://doi.org/10.1016/S0016-7037(97)00011-2

Dursun, N., Özcan, M. M., Kaşık, G., & Öztürk, C. (2006). Mineral contents of 34 species of edible mushrooms growing wild in Turkey. *Journal of the Science of Food and Agriculture, 86*(7), 1087-1094. doi:10.1002/jsfa.2462

Eriksson, J. (2001). *Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertiliser, precipitation and in oil and crops.* Retrieved from http://www.naturvardsverket.se/Documents/publikationer/620-6246-8.pdf

ESPI Metals. (2015). *Gallium.* Retrieved from http://www.espimetals.com/index.php/msds/135-Gallium%202015

ESPI Metals. (2016). *Indium.* Retrieved from http://www.espimetals.com/index.php/msds/146-Indium%202016

Essén, S. A., Johnsson, A., Bylund, D., Pedersen, K., & Lundstrom, U. S. (2007). Siderophore production by Pseudomonas stutzeri under aerobic and anaerobic conditions. *Applied and Environmental Microbiology, 73*(18), 5857–5864. doi:10.1128/AEM.00072-07

Eticha, D., Angelika, S., & Horst, W. J. (2005). Cell-wall pectin and its degree of methylation in the maize root-apex: significance for genotypic differences in aluminium resistance. *Plant, Cell & Environment, 28*(11), 1410-1420. doi:10.1111/j.1365-3040.2005.01375.x

Fischer, L., Brümmer, G. W., & Barrow, N. J. (2007). Observations and modelling of the reactions of 10 metals with goethite: Adsorption and diffusion processes. *European Journal of Soil Science, 58*(6), 1304-1315. doi:10.1111/j.1365-2389.2007.00924.x

Goldberg, S. (1997). Reactions of boron with soils. *Plant and Soil, 193*(1-2), 35-48. Retrieved from https://link-springer-com.ezproxy.lincoln.ac.nz/article/10.1023/A%3A1004203723343

Greenwood, N. N., & Earnshaw, A. (1984). *Chemistry of the elements.* Pergamon Press Ltd.

Grzybkowski, W. (2006). Nature and properties of metal cations in aqueous solutions. *Polish Journal of Environmental Studies, 15*(4), 655-663. Retrieved from http://www.6csnfn.pjoes.com/pdf/15.4/655-663.pdf

GSMArena. (2010). *Mobile phone evolution: Story of shapes and sizes.* Retrieved from https://www.gsmarena.com/mobile_phone_evolution-review-493p6.php

Gustafsson, J. P. (2013). *Visual MINTEQ ver. 3.1.* http://vminteq.lwr.kth.se

Ha, N. T. H., Sakakibara, M., Sano, S., & Nhuan, M. T. (2011). Uptake of metals and metalloids by plants growing in a lead–zinc mine area, Northern Vietnam. *Journal of Hazardous Materials, 186*(2-3), 1384-1391. doi:10.1016/j.jhazmat.2010.12.020

Hines, C. J., Roberts, J. L., Andrews, R. N., Jackson, M. V., & Deddens, J. A. (2013). Use of and occupational exposure to indium in the United States. *Journal of Occupational and Environmental Hygiene, 10*(12), 723-733. doi:10.1080/15459624.2013.836279

Hou, H., Takamatsu, T., Koshikawa, M., & Hosomi, M. (2005). Migration of silver, indium, tin, antimony, and bismuth and variations in their chemical fractions on addition to uncontaminated soils. *Soil Science, 170*(8), 624-639. doi:10.1097/01.ss.0000178205.35923.66

Hooda, P. S. (2010). *Trace elements in soils.* Blackwell Publishing Ltd.

Horst, W. J., Wang, Y., & Eticha, D. (2010). The role of the root apoplast in aluminium-induced inhibition of root elongation and in aluminium resistance of plants: A review. *Annals of Botany, 106*(1), 185–197. doi:10.1093/aob/mcq053

Ishikawa, S., Wagatsuma, T., & Ikarashi, T. (1996). Comparative toxicity of Al3+, Yb3+, and La3+ to root-tip cells differing in tolerance to high Al3+ in terms of ionic potentials of dehydrated trivalent cations. *Soil Science and Plant Nutrition, 42*(3), 613-625. doi:10.1080/00380768.1996.10416330

Ivanoff, C. S., Ivanoff, A. E., & Hottel, T. L. (2012). Gallium poisoning: A rare case report. *Food and Chemical Toxicology, 50*(2), 212-215. https://doi.org/10.1016/j.fct.2011.10.041

Jaskula, B. W. (2016). *Gallium.* Retrieved from https://minerals.usgs.gov/minerals/pubs/commodity/gallium/mcs-2016-galli.pdf

Johnson, G. V., & Burton, L. L. (2007). Inhibition of iron deficiency stress response in cucumber by rare earth elements. *Plant Physiology and Biochemistry, 45,* 302-308. doi:10.1016/j.plaphy.2007.03.012

Kabata-Pendias, A., & Pendias, H. (2001). *Trace elements in soils and plants.* Retrieved from http://base.dnsgb.com.ua/files/book/Agriculture/Soil/Trace-Elements-in-Soils-and-Plants.pdf

Kabata-Pendias, A., & Mukherjee, A. (2007). *Trace elements from soil to human.* Springer.

Kelson, A. B., Carnevali, M., & Truong-Le, V. (2013). Gallium-based anti-infectives: targeting microbial iron-uptake mechanisms. *Current Opinion in Pharmacology, 13*(5), 707-716. https://doi.org/10.1016/j.coph.2013.07.001

Kinraide, T. B. (1997). Reconsidering the rhizotoxicity of hydroxyl, sulphate, and fluoride complexes of aluminium. *Journal of Experimental Botany, 48*(5), 1115–1124. https://doi-org.ezproxy.lincoln.ac.nz/10.1093/jxb/48.5.1115

Kochian, L. V., Hoekenga, O. A., & Pineros , M. A. (2004). How do crop plants tolerate acid soils? Mechanisms of aluminum tolerance and phosphorous efficiency. *Annual review of plant biology, 55*(1), 459-493. doi:10.1146/annurev.arplant.55.031903.141655

Kopittke, P. M., McKenna, B. A., Blamey, F. P. C., Wehr, J. B., & Menzies, N. W. (2009). Metal-induced cell rupture in elongating roots is associated with metal ion binding strengths. *Plant and Soil, 322*(1-2), 303–315. doi:10.1007/s11104-009-9917-0

Kopittke, P. M., Menzies, N. W., Wang, P., & Blamey, F. (2016). Kinetics and nature of aluminium rhizotoxic effects: a review. *Journal of Experimental Botany, 67*(15), 4451–4467. https://doi-org.ezproxy.lincoln.ac.nz/10.1093/jxb/erw233

Ladenberger, A., Demetriades, A., Reimann, C., Birke, M., Sadeghi, M., Uhlbäck, J., … Jonsson, E. (2015). GEMAS: Indium in agricultural and grazing land soil of Europe — Its source and geochemical distribution patterns. *Journal of Geochemical Exploration, 154,* 61-80. https://doi.org/10.1016/j.gexplo.2014.11.020

Lin, C., Chang, K., Tsay, C., Lee, D., Lo, S., & Yasunga, T. (1997). Adsorption mechanism of Gallium(III) and Indium(III) onto γ-Al2O3. *Journal of Colloid and Interface Science, 188,* 201-208. doi:10.1006/jcis.1996.4739

Lokanc, M., Eggert, R., & Redlinger, M. (2015). *The availability of indium: The present, medium term, and long term.* Retrieved from https://www.nrel.gov/docs/fy16osti/62409.pdf

Luda, M. P. (2011). Recycling of printed circuit boards. In S. Kumar (Ed.*), Integrated Waste Management - Volume II* (pp. 285-298). doi:10.5772/17220

McLaren, R. G., & Cameron, K. C. (1996). *Soil science.* Oxford university press.

Maneesuwannarat, S., Teamkao, P., Vangnai, A. S., Yamashita, M., & Thiravetyan, P. (2016). Possible mechanism of gallium bioleaching from gallium nitride (GAN) by Arthrobacter creatinolyticus: Role of amino acids/peptides/proteins bindings with gallium. *Process Safety and Environmental Protection, 103*(A), 36-45. https://doi.org/10.1016/j.psep.2016.06.036

Maneesuwannarat, S., Vangnai, A. S., Yamashita, M., & Thiravetyan, P. (2016b). Bioleaching of gallium from gallium arsenide by Cellulosimicrobium funkei and its application to semiconductor/electronic wastes. *Process Safety and Environmental Protection, 99,* 80-87. https://doi.org/10.1016/j.psep.2015.10.008

Martin, W. C., Musgrove, A., Kotochigova, S., & Sansonetti, J. E. (2013). *Ground levels and ionization energies for the neutral atoms.* Retrieved from https://www.nist.gov/pml/ground-levels-and-ionization-energies-neutral-atoms

Mauseth, J. D. (2014). *Botany: An introduction to plant biology* (fifth edition). Burlington, MA: Jones & Bartlett Learning.

Ministry of Health. (2008). *Drinking-water standards for New Zealand 2005 (revised 2008).* Retrieved from https://www.health.govt.nz/system/files/documents/publications/drinking-water-standards-2008-jun14.pdf

NIWA. (n.d.). *Mean 10cm earth temperature (°C).* Retrieved from https://www.niwa.co.nz/education-and-training/schools/resources/climate/earthtemp

Oguchi, M., Murakami, S., Sakanakura, H., Kida, A., & Kameya, T. (2011). A preliminary categorization of end-of-life electrical and electronic equipment as secondary metal resources. *Waste Management, 31*(9-10), 2150-2160. Retrieved from https://doi.org/10.1016/j.wasman.2011.05.009

Pearson, R. G. (1963). Hard and soft acids and bases. *Journal of the American Chemical Society, 85*(22), 3533-3539. doi:10.1021/ja00905a001

Pestana, M., Correia, P. J., Saavedra, T., Gama, F., Dandlen, S., Nolasco, G., de Varennes, A. (2013). Root ferric chelate reductase is regulated by iron and copper in strawberry plants. *Journal of Plant Nutrition, 36*(13), 2035-2047. doi:10.1080/01904167.2013.816731

Pokrovski, G. S., Diakonov, I. I., Bénézeth, P., Gurevich, V. M., Gavrichev, K. S., Gorbunov, V. E., … Khodakovsky, , I. L. (1997). Thermodynamic properties of gallium hydroxide oxide (α-GaOOH) at temperatures to 700 K. *European Journal of Mineralogy, 9,* 941-951. Retrieved from https://www.researchgate.net/publication/259465458_Thermodynamic_Properties_of_Gallium_Hydroxide_Oxide_-GaOOH_at_Temperatures_to_700_K

Pokrovski, G. S., Schott, J., Hazemann, J., Farges, F., & Pokrosky, O. S. (2002). An X-ray absorption fine structure and nuclear magnetic resonance spectroscopy study of gallium–silica complexes in aqueous solution. *Geochimica et Cosmochimica Acta, 66*(24), 4203-4222. Retrieved from https://hal.archives-ouvertes.fr/hal-00076917/document

Połedniok, J. (2007). A sensitive spectrophotometric method for determination of trace quantities of indium in soil. *Water, Air, and Soil Pollution, 186*(1), 343-349. doi:10.1007/s11270-007-9491-0

Połedniok, J. (2012). Speciation of scandium and gallium in soil. *Chemosphere, 73*(4), 572-579. https://doi.org/10.1016/j.chemosphere.2008.06.012

Połedniok, J., Kita, A., & Zerzucha, P. (2012). Spectrophotometric and inductively coupled plasma–optical emission spectroscopy determination of gallium in natural soils and soils polluted by industry: Relationships between elements. *Communications in Soil Science and Plant Analysis, 43*(8), 1121-1135. doi:10.1080/00103624.2012.662561

Reeder, S., Taylor, H., Shaw, R. A., & Demetriades, A. (n.d.). *Introduction to the chemistry and geochemistry of the elements.* Retrieved from http://weppi.gtk.fi/publ/foregsatlas/articles/Chemistry.pdf

Reid, R. J., Smith, Z., & Rengel, F. A. (1996). Membrane fluxes and comparative toxicities of aluminium, scandium and gallium. *Journal of Experimental Botany, 47*(305), 1881-1888. https://doi.org/10.1093/jxb/erx351

Ritchie, R. J., & Raghupathi, S. S. (2008). Al-toxicity studies in yeast using gallium as an aluminium analogue. *BioMetals, 21*(4), 379-393. doi:10.1007/s10534-007-9127-2

Robinson, N. J., Procter, C. M., Connolly, E. L., & Guerinot, M. L. (1999). A ferric-chelate reductase for iron uptake from soils. *Nature, 397*(6721), 694-697. http://dx.doi.org.ezproxy.lincoln.ac.nz/10.1080/01904167.2013.816731

Robinson, B. H. (2009). E-waste: An assessment of global production and environmental impacts. *Science of The Total Environment, 408*(2), 183-191. https://doi.org/10.1016/j.scitotenv.2009.09.044

Römheld, V. (1987). Different strategies for iron acquisition in higher plants. *Physiologia Plantarum, 2,* 231-234. doi:10.1111/j.1399-3054.1987.tb06137.x

Rongguo, C., Juan, G., Liwen, Y., Huy. D., & Liedtke, M. (2016). *Supply and demand of lithium and gallium.* Retrieved from https://www.bgr.bund.de/EN/Themen/Min_rohstoffe/Downloads/studie_Li_Ga.pdf?__blob=publicationFile&v=4

Rühling, Å., & Tyler, G. (2004). Changes in the atmospheric deposition of minor and rare elements between 1975 and 2000 in south Sweden, as measured by moss analysis. *Environmental Pollution, 131*(3), 417-423. doi:10.1016/j.envpol.2004.03.005

Ryan, P. (2014). *Environmental and low temperature geochemistry.* Retrieved from https://ebookcentral.proquest.com/lib/lincoln-ebooks/reader.action?docID=1673977

Salminen, R. (n.d.). *Gallium.* Retrieved from http://weppi.gtk.fi/publ/foregsatlas/text/Ga.pdf

Salminen, R. (n.d.b). *Indium.* Retrieved from http://weppi.gtk.fi/publ/foregsatlas/text/In.pdf

Schulte, R. F., & Foley, N. K. (2013). *Compilation of gallium resource data for bauxite deposits.* Retrieved from https://pubs.usgs.gov/of/2013/1272/pdf/ofr2013-1272.pdf

Schwarz-Schampera, U. (2014). *Indium.* In G. Gunn (Ed.), Critical metals handbook (pp. 204-229). Retrieved from https://ebookcentral.proquest.com/lib/lincoln-ebooks/reader.action?docID=1594545

Shaheen, S. M., Tsadilas, C. D., & Rinklebe, J. (2013). A review of the distribution coefficients of trace elements in soils: Influence of sorption system, element characteristics, and soil colloidal properties. *Advances in Colloid and Interface Science, 201-202,* 43-56. https://doi.org/10.1016/j.cis.2013.10.005

Shaheen, S. M., Tsadilas, C. D., Rupp, H., Rinklebe, J., & Meissner, R. (2015). Distribution coefficients of cadmium and zinc in different soils in mono-metal and competitive sorption systems. *Journal of Plant Nutrition and Soil Science, 178*(4), 671-681. doi:10.1002/jpln.201400475

Shannon, R. R. (1976). Revised effective ionic radii and systematic study of inter atomic distances in halides and chalcogenides. *Acta crystallographica. Section A, Foundations of crystallography, 32,* 751-767. doi:10.1107/s0567739476001551

Sheppard, M.I., Sheppard, S.C., & Grant, C. A. (2007). Solid/liquid partition coefficients to model trace element critical loads for agricultural soils in Canada. *Canadian Journal of Soil Science, 87*(2), 189-201. https://doi.org/10.4141/S06-061

Sheppard, S., Long, J., Sanipelli, B., & Sohlenius, G. (2009). *Solid/liquid partition coefficients (Kd) for selected soils and sediments at Forsmark and Laxemar-Simpevarp.* Retrieved from http://www.skb.com/publication/1951648/R-09-27.pdf

Sheppard, S., Sohlenius, G., Omberg, L., Borgiel, M., Grolander, S., & Nordén, S. (2011). *Solid/liquid partition coefficients (Kd) and plant/soil concentration ratios (CR) for selected soils, tills and sediments at Forsmark.* Retrieved from http://www.skb.se/upload/publications/pdf/r-11-24.pdf

Shiller, A. M., & Frilot, D. M. (1996). The geochemistry of gallium relative to aluminum in Californian streams. *Geochimica et Cosmochimica Acta, 60*(8), 1323-1328. https://doi.org/10.1016/0016-7037(96)00002-6

Snowden, K. C., Richards, K. D., & Gardner, R. C. (1995). Aluminum-induced genes (induction by toxic metals, low calcium, and wounding and pattern of expression in root tips). *Plant Physiology, 107*(2), 341-348. https://doi-org.ezproxy.lincoln.ac.nz/10.1104/pp.107.2.341

Sohlenius, G., Saetre, P., Nordén, S., Grolander, Sara., & Sheppard, S. (2013). Inferences about radionuclide mobility in soils based on the solid/liquid partition coefficients and soil properties. *AMBIO, 42*(4), 414-424. doi:10.1007/s13280-013-0408-4

Staff, K., Brown, M. B., Hider, R. C., Kong, X. L., Friden, P., & Jones, S. A. (2010). Recovering Ga(III) from coordination complexes using pyridine 2,6-dicarboxylic acid chelation ion chromatography. *Biomedical Chromatography, 24*(9), 1015-1022. doi:10.1002/bmc.1402

Statista. (2017). *Shipment forecast of laptops, desktop PCs and tablets worldwide from 2010 to 2021 (in million units).* Retrieved from https://www.statista.com/statistics/272595/global-shipments-forecast-for-tablets-laptops-and-desktop-pcs/

Steinberger, H. (1998). Health, safety and environmental risks from the operation of CdTe and CIS thin-film modules. *Progress in Photovoltaics: Research and Applications, 6*(2), 99-103. doi: 10.1002/(SICI)1099-159X(199803/04)6:2<99::AID-PIP211>3.0.CO;2-Q

Sterckeman, T., Douay, F., Proix, N., Fourrier, H., & Perdrix, E. (2002). Assessment of the contamination of cultivated soils by eighteen trace elements around smelters in the north of France. *Water, Air, and Soil Pollution, 135*(1), 173-194. http://dx.doi.org.ezproxy.lincoln.ac.nz/10.1023/A:1014758811194

Stumm, W., & Morgan, J. J. (2009). *Aquatic chemistry : Chemical equilibria and rates in natural waters.* Retrieved from https://ebookcentral.proquest.com/lib/lincoln-ebooks/reader.action?docID=1550541#

Syu, C., Chien, P., Huang, C., Jiang, P., Juang, K., & Lee, D. (2017). The growth and uptake of Ga and In of rice (*Oryza sative* L.) seedlings as affected by Ga and In concentrations in hydroponic cultures. *Ecotoxicology and Environmental Safety, 135,* 32-39. https://doi.org/10.1016/j.ecoenv.2016.09.016

Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry, 51*(7), 844–851. doi:10.1021/ac50043a017

Tolcin, A. C. (2017). *Indium.* Retrieved from https://minerals.usgs.gov/minerals/pubs/commodity/indium/mcs-2017-indiu.pdf

Tuck, D. G. (1983). Critical survey of stability constants of complexes of indium. *Pure and Applied Chemistry, 55*(9), 1477-1528. Retrieved from http://old.iupac.org/publications/pac/1983/pdf/5509x1477.pdf

Tyler, G. (2004a). Ionic charge, radius, and potential control root/soil concentration ratios of fifty cationic elements in the organic horizon of a beech (Fagus sylvatica) forest podzol. *Science of The Total Environment, 329*(1-3), 231-239. https://doi.org/10.1016/j.scitotenv.2004.03.004

Tyler, G. (2004b). Vertical distribution of major, minor, and rare elements in a Haplic Podzol. *Geoderma, 119*(3-4), 277-290. https://doi.org/10.1016/j.geoderma.2003.08.005

Tyler, G. (2005). Changes in the concentrations of major, minor and rare-earth elements during leaf senescence and decomposition in a Fagus sylvatica forest. *Forest Ecology and Management, 206*(1-3), 167-177. https://doi.org/10.1016/j.foreco.2004.10.065

Tyler, G., & Olsson, T. (2001). Concentrations of 60 elements in the soil solution as related to the soil acidity. *European Journal of Soil Science, 52*(1), 151-165. doi:10.1046/j.1365-2389.2001.t01-1-00360.x

Tyler, G., & Olsson, T. (2002). Conditions related to solubility of rare and minor elements in forest soils. *Journal of Plant Nutrition and Soil Science, 165*(5), 594-601. doi:10.1002/1522-2624(200210)165:5<594::AID-JPLN594>3.0.CO;2-K

USGS. (2017). *Mineral commodity summaries 2017.* Retrieved from https://minerals.usgs.gov/minerals/pubs/mcs/2017/mcs2017.pdf

Valentinuzzi, F., Mimmo, T., Cesco, S., Al Mamun, S., Santner, J., Hoefer, C., … Lehto, N. (2015). The effect of lime on the rhizosphere processes and elemental uptake of white lupin. *Environmental and Experimental Botany, 118,* 85-94. https://doi.org/10.1016/j.envexpbot.2015.06.010

Violante, A., Ricciardella, M., Pigna, M., & Capasso, R. (2005). Chapter 5 – Effects of organic ligands on the adsorption of trace elements onto metal oxides and organo-mineral complexes. In P. M. Huang & G. R. Gobran (Eds.), *Biogeochemistry of trace elements in the rhizosphere* (pp. 204-229). https://doi-org.ezproxy.lincoln.ac.nz/10.1016/B978-044451997-9/50007-6

Waterlot, C., Bidar, G., Pelfrëne, A., Roussel, H., Fourrier, H., & Douay, F. (2013). Contamination, fractionation and availability of metals in urban soils in the vicinity of former lead and zinc smelters, France. *Pedosphere, 23*(2), 143-159. https://doi.org/10.1016/S1002-0160(13)60002-8

Watmough, S. (2008). Element mobility and partitioning along a soil acidity gradient in central Ontario forests, Canada. *Environmental Geochemistry and Health, 30*(5), 431-444. doi: 10.1007/s10653-007-9127-8

Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica et Cosmochimica Acta, 59*(7), 1217-1232. https://doi.org/10.1016/0016-7037(95)00038-2

Weeks, R. A. (1973). Gallium, geranium and indium. In D. A. Brobst & W. P. Pratt (Eds.), *Geological survey professional paper: Issue 820* (pp. 237-246). U.S. Government Printing Office.

White, S. J. O., & Hemond, H. F. (2012). The anthrobiogeochemical cycle of indium: A review of the natural and anthropogenic cycling of indium in the environment. *Critical Reviews in Environmental Science and Technology, 42*(2), 155-186. doi:10.1080/10643389.2010.498755

Wong, J.W.C., Ip, C.M., & Wong, M.H. (1998). Acid-forming capacity of lead-zinc mine tailings and its implications for mine rehabilitation. *Environmental Geochemistry and Health, 20*(3), 149-155. Retrieved from https://link-springer-com.ezproxy.lincoln.ac.nz/article/10.1023/A%3A1006589124204

Wood, S. A., & Samson, I. M. (2006). The aqueous geochemistry of gallium, germanium, indium and scandium. *Ore Geology Reviews, 28*(1), 57-102. https://doi.org/10.1016/j.oregeorev.2003.06.002

Yu, X., Feng, X., & Feng, Y. (2015). Phytotoxicity and Transport of Gallium (Ga) in Rice Seedlings for 2-Day of Exposure. *Bulletin of Environmental Contamination and Toxicology, 95*(1), 122-125. doi:10.1007/s00128-015-1471-2